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Biogenic Emission Measurements from Birch and Spruce Trees using Vocus PTR-TOF

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Tiivistelmä — Referat — Abstract

Biogenic Volatile Organic Compounds play a major role in the atmosphere by acting as precursors in the formation of secondary organic aerosols and by also affecting the concentration of ozone. The chemical diversity of BVOCs is vast but global emissions are dominated by isoprene and monoterpenes. The emissions of BVOCs from plants are affected by environmental parameters with temperature and light having significant impacts on the emissions. The Downy birch and Norway spruce trees consist of heavy and low volatile compounds but published results are limited up to observing sesquiterpenoid emissions from these two trees. In this study, the Vocus proton-transfer-reaction time-of-flight mass spectrometer is deployed in the field to examine BVOC emissions from Downy birch and Norway spruce trees. With higher mass resolution, shorter time response and lower limits of detection than conventional PTR instruments, the Vocus can effectively measure a broader range of VOCs. For the first time, real-time emissions of diterpenes and 12 different oxygenated compounds were observed from birch and spruce trees. The emission spectrum of birch was dominated by $C_{10}H_{17}^+$, while for spruce $C_5H_9^+$ contributed the most. The sum emissions of oxygenated compounds contributed significantly to the observed total emissions from both the trees. The emission rates of all compounds varied dramatically throughout the period due to fluctuations in temperature and light. Due to lack of data from spruce, conclusive results for temperature and light response on terpene emissions could not be drawn. For birch, the emission rates were well explained by the temperature and temperature-light algorithms. The terpene emissions modelled using both algorithms correlated similarly with experimental data making it difficult to decisively conclude if the emissions originated from synthesis or pools.

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BVOC, Vocus, Birch, Spruce, Monoterpenes, Sesquiterpenes, Diterpenes, OVOCs

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Contents

Abbreviations

VOC: Volatile Organic Compound

BVOC: Biogenic Volatile Organic Compound

GLV: Green Leaf Volatile

HOM: Highly Oxygenated Molecule

SOA: Secondary Organic Aerosol

PTR-ToF-MS: Proton-transfer-reaction time-of-flight mass spectrometer

PA: Proton Affinity

FIMR: Focusing Ion-Molecule Reactor

PAR: Photosynthetic Active Radiation

RH: Relative Humidity

T-algorithm: Temperature algorithm

TL-algorithm: Temperature-Light algorithm

E_T: Emission potential calculated using T-algorithm

E_{TL}: Emission potential calculated using TL-algorithm

MEK: Methyl Ethyl Ketone

MVK: Methyl Vinyl Ketone

MAC: Methacrolein

1. Introduction

The US Environmental Protection agency defines Volatile Organic Compounds (VOC) as the class of compounds containing carbon atoms excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates and ammonium carbonate which participates in atmospheric photochemical reactions (X. Zhang et al., 2017). They include a broad spectrum, which are classified based on their structure, type of functional group and type of bond. The sources of VOCs can be either natural or anthropogenic. Anthropogenic VOC emissions are becoming worse as daily human activities such as cooking, driving, construction, painting, breathing result in the emissions of VOCs (Koppmann, 2007; X. Zhang et al., 2017). However, the major contribution of human-induced VOC emissions are from the use of fossil fuels (X. Zhang et al., 2017). Human-induced VOC emissions vary between 100 and 160 TgC yr^{-1} (Chen et al., 2019).

The biosphere also naturally emits VOCs into the atmosphere and are known as biogenic volatile organic compounds (BVOCs). Generally, BVOCs are referred to the organic compounds emitted from terrestrial vegetation and they contribute 90% of total global VOC emissions (Matsunaga et al., 2011). Globally, the BVOC emissions are an order of magnitude higher than anthropogenic emissions with an estimate of 1000 TgC yr^{-1} (Guenther et al., 2012; Simon et al., 2001). They are diverse and include terpenoids, alkanes, alkenes, alcohols, esters, carbonyls and acids (Peñuelas and Llusià, 2003,Haberstroh et al., 2018). The terpenes namely isoprene, monoter-

penes and sesquiterpenes together contribute the largest fraction to the global BVOC emissions (Guenther et al., 2012). All organs of the plants from flowers to roots can emit BVOCs in varying quantities and chemical composition with greatest emissions seen from leaves (Šimpraga et al., 2019; Laothawornkitkul et al., 2009). However, substantial emissions of BVOCs especially terpenoids have been observed from bark and wood of trees such as conifers (Šimpraga et al., 2019). Even trees such as birch have complex chemical compounds in their leaves and bark, although emissions from bark of birch have not been reported (Abyshev et al., 2007; Peltonen et al., 2005).

The reason as to why plants emit BVOCs is still a matter of debate for the scientific community. Plants sometime emit up to 10%, a significant fraction of their assimilated carbon into the atmosphere (Loreto et al., 2014; Peñuelas and Llusià, 2003). However, by releasing BVOCs, plants carry out certain functions like communicating with pollinators, herbivory predators or even other plants and organisms (Fineschi et al., 2013; Šimpraga et al., 2016; Faiola and Taipale, 2020). The plants also emit BVOCs as a response to multiple stress factors such as heat, ozone, drought and also other biotic stresses such as insects and pathogens, to name a few (Šimpraga et al., 2019; Gouinguené and Turlings, 2002; Kari et al., 2019). For example, isoprene protects the plants against reactive oxygenated species and prevents cell death (Vickers et al., 2009; Loreto, Mannozzi, et al., 2001). In nature, plants are exposed to multiple stresses periodically, while this can result in the induction of new compounds, it can also have an additive effect on BVOC emissions (Blande et al., 2014; Holopainen and Gershenzon, 2010).

As BVOCs are highly reactive compounds, their lifetimes in the atmosphere vary from seconds to days (Atkinson and Arey, 2003). The BVOCs play an important role in atmospheric chemistry and physics. When BVOCs are released to the atmosphere, they undergo oxidation and form various oxygenated products that ultimately lead to the production of carbon-dioxide and water (H. Li, Väliranta,

et al., 2020, Laothawornkitkul et al., 2009). However, during this process these BVOCs can give rise to the formation of atmospheric particles called secondary organic aerosols (SOA) in the presence of OH, O_3 or NO_3 (Monson, 2010; Borbon et al., 2013; Shrivastava et al., 2017). Also, it has been observed that BVOCs yield low volatile highly oxygenated molecules that further enhance the formation of SOA (Bianchi et al., 2019). The aerosols formed can influence cloud formation and also impact the earth's radiation budget (Faiola and Taipale, 2020). BVOCs make up the largest fraction (70%-95%) of precursors for the formation of SOA (Kelly et al., 2018). BVOCs also act as a source and sink for tropospheric ozone and OH radicals and significantly affect the atmospheric composition (Šimpraga et al., 2019). The BVOCs affect the atmosphere-biosphere interactions significantly and maintain the health and functionality of the ecosystem.

The aim of this study is to characterise and quantify BVOC emissions from Betula pubescens (Downy birch) and Picea abies (Norway spruce) using Vocus proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF). With both trees being rich in complex and low volatile compounds (Abyshev et al., 2007; D. Martin et al., 2002), a question arises whether these compounds are emitted into the atmosphere. Studies that have observed BVOC emissions from these two trees have reported only highly volatile compounds. Moreover, studies with regard to BVOC emissions from birch are limited in number. Due to improved measurement technique, the Vocus can measure a broader range of compounds compared to conventional PTR instruments (Krechmer et al., 2018) and hence, this research will provide new insights into BVOC emissions from birch and spruce trees. The following questions are also addressed in this thesis: 1) How do emission potentials of terpenes in this study compare to the published results? 2) How do the observed emissions depend on light and temperature by fitting the measured data to the light and/or temperature algorithm formulated by Guenther et al. (1993)?

2. Background

2.1 Biogenic Volatile Organic Compounds

Biogenic Volatile Organic Compounds (BVOCs) have been given prominence since the 1960s. Vegetation emits a vast number of chemicals into the atmosphere, all of which are important to the functioning of the ecosystem. Between the years 1970 and 2000, more than 150 studies were published with regard to BVOCs, with quite a number of them concluding that BVOCs do not influence air quality. However, later numerous studies were published regarding the importance of BVOCs especially in the formation of secondary organic aerosols, which caught the interest of the scientific community. Since then, several air quality and climate models have included BVOC emissions from different vegetation types. Eventually, it led to the development of a very comprehensive emission model called the Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1) that gives annual biogenic emissions for 147 different compounds from the terrestrial ecosystem (Guenther, 2013).

BVOC emissions from terrestrial vegetation form the largest source of VOCs in the atmosphere. These BVOCs perform several functions in the ecosystem, such as defence against predators, plant-plant signalling, plant-pathogen interaction, pollinator attraction and environmental stress signalling (J. S. Yuan et al., 2009). Because of their high concentration in the atmosphere, they influence the oxidation levels of the troposphere, global carbon cycle (Guenther et al., 1995) and aerosol concentration (Hoffmann et al., 1997). Hence, the important BVOCs, such as monoterpenes

and isoprene, which are abundant in the atmosphere (65% of BVOCs emitted from terrestrial vegetation) (Harrison et al., 2013; Acosta Navarro et al., 2014; Hantson et al., 2017) are included in atmospheric chemistry, air quality and earth system models with enormous uncertainties in their emission levels (Guenther et al., 2012). Characterization of BVOCs is one of the major difficulties faced and their identification in the atmosphere is improving with the development of the measurement techniques and instruments (H. Li, Riva, et al., 2020; Matsunaga et al., 2011; Guenther et al., 2012).

2.2 Terpenoid Compounds

Among the BVOCs present in the atmosphere, terpenes form the largest contribution of BVOC emissions from terrestrial vegetation (Guenther et al., 2012). The basic terpene consists of a five-carbon unit $(C_5H_8)_n$ (where 'n' is the number of units) in varied forms with several alterations in their chemical formula. The rest of the terpenes are a continuous build of the basic C5 block with alterations in structure and attached functional groups. The terpenoids can be further classified as hemiterpenes (n=1), monoterpenes (n=2), sesquiterpenes (n=3), diterpenes (n=4) triterpenes (n=6) and so on (Vickers et al., 2009). Being immobile, plants need a way to communicate with several organisms. Terpenes are responsible for the plant-plant interaction, plant-insect interation and they act as plant-defense against predators.

Terpenenoids are produced in plants through two routes or metabolic pathways: the cytosolic mevalonic acid (MVA) pathway and the plastidic 2-C-methyl-D-erythritol 4-phosphate (MEP) pathway (Vickers et al., 2009; Haberstroh et al., 2018). The MEP and MVA pathways are responsible for cell growth and maintenance and occur in all plants. It was found that hemiterpenes, monoterpenes and diterpenes are formed from the MEP pathway, while sesquiterpene is formed from MVA pathway (Vickers et al., 2009); other studies have mentioned evidences of ex-

change of metabolites between the two pathways (Yang et al., 2012). In a significant study, Dudareva et al. (2005) found that certain sesquiterpenes were formed from the MEP pathway and not MVA. The highest numbers of compounds emitted from plants in the terpene family are isoprenes, monoterpenes and sesquiterpenes. These compounds have a very high vapour pressure, which allows them to be released very easily at environmental temperatures (Vickers et al., 2009; Haberstroh et al., 2018).

2.2.1 Isoprene

Isoprene dominates the BVOC emission from terrestrial vegetation into the atmosphere (Guenther, 2013; Kanakidou et al., 2005; Acosta Navarro et al., 2014) and has been studied comprehensively than all other BVOCs. Isoprene is a very important antioxidant and plants with emissions of isoprene prove to cope better in stressful conditions. The accumulation of reactive oxygen species (HO_2, O, OH) is known to cause cell death. Isoprene has proved to act as a defence mechanism for plants to protect the plant tissues against several environmental stress factors such as temperature and reactive oxygen species (Vickers et al., 2009; Shrivastava et al., 2017), but is seen to react less against herbivory attack (Loivamaki et al., 2008). However, it is shown shown that isoprene emitted from tobacco plants deterred caterpillars from feeding (Laothawornkitkul et al., 2008). Once emitted, isoprene, due to its high reactivity (Kuhn et al., 2002), instantly undergoes chemical reactions with O_3, OH and NO_3 that are abundant in the atmosphere. During its oxidation, isoprene gives rise to methyl ethyl ketone (MEK), methyl vinyl ketone (MVK) and methacrolein (MAC), which are by itself highly reactive. (Pierotti et al., 1990). These products were initially thought to be not emitted naturally as shown by Pierotti et al. (1990) where MAC and MVK are not directly emitted from California live oaks. Later, a study in 2005 showed that plants are capable of bidirectional exchange of MVK (Karl et al., 2005). Recent studies have shown direct emissions of MVK and MAC from plants (Jardine et al., 2011; Jardine et al., 2013; Cappellin et al., 2019), while

Jardine et al. (2011) reported on the mechanism for the production of MEK within plants.

2.2.2 Monoterpenes

Monoterpenes are another diverse class of compounds which consist of two isoprene units. They are stored in specialised storage sacs called resin ducts which react to the temperature levels, while plants without the presence of storage structures emit monoterpenes with response to light and temperature (Staudt and Bertin, 1998; Loreto et al., 2000). Monoterpenes have also been emitted as a response to biotic and abiotic stress (Niederbacher et al., 2015). The atmospheric chemistry of monoterpenes is very much similar to that of isoprene and is widely analysed as much as isoprene due to its abundance in the atmosphere. Monoterpenes also act as precursors in photochemical ozone production at high NOx levels but at the same time act as ozone sinks in low NOx environments (Arneth et al., 2008). Monoterpenes act as much more significant precursors in the formation of secondary organic aerosols in the atmosphere than isoprenes (Arneth et al., 2008), and also have a higher reactivity with OH radicals and ozone (Papiez et al., 2009). Bianchi et al. (2019) gave an in-depth review regarding the formation of highly oxygenated molecules (compounds containing atleast 6 oxygen atoms) from monoterpenes. The formation of these very low volatile compounds gives rise to SOA and new particle formation. Furthermore, monoterpenes have been identified to have emitted also from anthropogenic sources such as traffic and wood combustion (Hellén et al., 2012).

2.2.3 Sesquiterpenes

Sesquiterpenes are mostly emitted from broad-leaved trees and are important precursors for secondary organic aerosols. Sesquiterpenes are rather difficult to detect than monoterpenes due to the fact that they have higher reactivity (Guenther, 2013). Sesquiterpenes have been reported to have high yields of SOA, even up to 100%

Table 2.1: Chemical Lifetimes of the most common terpenoids emitted from plants which are estimated with certain concentrations of NO_2, O_3 and OH and the global emissions from natural sources.(Acosta Navarro et al., 2014)

Compounds (Formula)	Chemical Lifetime	Global Emissions (TgC/yr)
Isoprene (C_5H_8)	Hours	309-706
Monoterpene ($C_{10}H_x$)	Minutes to Hours	26-156
Sesquiterpenes ($C_{15}H_x$)	Less than 1 day	26

compared with other SOA precursors (Sakulyanontvittaya et al., 2009; Vizuete et al., 2004). Sesquiterpenes have been regarded as soldiers that protect the plants and even sponges (marine) from herbivory. These sesquiterpenes are a constituent of fragrance and essential oils in plants. The oxygenated sesquiterpenes present in fruits and vegetables have been reported to prevent cancer. Sesquiterpenes perform similar roles to monoterpenes in plants. An extensive review was published listing the possible roles sesquiterpenes and oxygenated sesquiterpenes play and the benefits of these compounds to human health (Chadwick et al., 2013). Emitted in lesser amounts than isoprene and monoterpenes, the functions of sesquiterpenes in the life cycle of a plant is important as these compounds constitute a large fraction of a plant's defense system.

2.2.4 Diterpenes

Diterpenes were thought of as compounds which were not emitted from plants due to their low volatility (Matsunaga et al., 2011). But these compounds have been identified to play a vital role in conifer defense against herbivory attack. These compounds harden on to the surface of a tree to seal the herbivory induced wound (Keeling and Bohlmann, 2006). Diterpenes play a major role in the plant defence against pathogens due to its antibiotic properties (Okada, 2011; Lu et al., 2018). Diterpenes

also function as antifeedants in the roots of plants and reduce root herbivory damage and hence, play a vital role in the belowground plant defence (Vaughan et al., 2013). Abietane acts as an important signalling compound that helps the organs of the plant to prepare itself against pathogens (Chaturvedi et al., 2012; Shah et al., 2016). There are around 12,000 diterpenes in plants, few of which have been identified to have important metabolic and physiological functions (Shah et al., 2016). Owing to recent advances in measurement techniques diterpene emissions have been observed from conifers in a study by Matsunaga et al. (2011) and also mediterranean shrubs conducted by Yáñez-Serrano et al. (2018). A study conducted by H. Li, Riva, et al. (2020) observed diterpenes in the ambient environment, while another study by H. Li, Väliranta, et al. (2020) observed diterpene emission from thawing permafrosts. Diterpenes are expected to have a high yield of aerosol formation due to its molecular weight and high reactivity, which is a result of its unsaturated structure (Matsunaga et al., 2011). However, there is limited information regarding its behaviour in the atmosphere due to the limitation to detect effectively (Yáñez-Serrano et al., 2018).

2.3 Other Prominent BVOCs

Acetone is an abundant oxygenated organic compound in the atmosphere. The terrestrial ecosystem contributes to around 37% of acetone emissions into the atmosphere and the vegetation alone emits 43.7 TgC yr^{-1} (Guenther et al., 2012; Guenther, 2013). With the addition to being abundant, acetone also has the longest lifetime among the carbonyl compounds in the atmosphere, having mean lifetime of about a month. Acetone is also a source of OH radicals in the upper atmosphere, which in turn reacts with acetone and other VOCs instantly.

Methanol is yet another BVOC that promotes plant growth, positively impact cell metabolism and protect the plants against insects, pathogens and physical damage. Methanol emitted is considered to act as an alarm for the neighbouring plants

to indicate injury and set up defence appropriately (Dorokhov et al., 2018). Its emissions are associated with pectin, one of the constituents that makes up the plant cell wall and hence is emitted by all plants (Harley et al., 2007; Dorokhov et al., 2018).

Benzenoid compounds are considered primarily to be anthropogenic and can be emitted from traffic, fuel, industries and solvents. Heiden et al. (1999) reported the first emissions of toluene from plants in huge quantities as a result of stress. The study also showed that toluene was emitted in small quantities under natural conditions. Misztal et al. (2015), using MEGAN2.1 model, calculated the annual global emissions of toluene, xylene and benzene to lie between 4 and 40 TgC yr^{-1}. Only a few benzenoids have been identified to be emitted from certain plants either as floral scents or in response to stress, despite the fact that a broad array is produced as plant metabolites. However, biogenic benzenoid emissions are comparable with global anthropogenic emission and hence the sources for these compounds need to be revised (Misztal et al., 2015). They are of considerable importance due to their involvement in the formation of secondary organic aerosols (Ng et al., 2007) and ozone (Na et al., 2005).

Green Leaf Volatiles (GLVs) are C6 compounds that cause the aromatic green scent of the leaves but are also known to be emitted in larger quantities when attacked or when under stress caused by abiotic factors (Copolovici et al., 2012; Guenther, 2013). GLVs are emitted very quickly from the plants when attacked. Due to their rapid production, GLVs are considered to be important in plant-plant communication especially to signal the initiation of defence against a pathogen or herbivory attack (Scala et al., 2013). Some of the most common GLV compounds found are hexanal, and 1-hexanol (Guenther, 2013; Scala et al., 2013). Plants also emit other specific BVOCs such as ethene, methyl salicylate and (E)-4,8–dimethyl–1,3,7-nonatriene (DMNT) that are emitted as a response to stress. The global annual emission rate calculated by Guenther et al. (2012) showed ethene to be at 26 TgC

yr^{-1} after terpenoids, acetone and methanol.

2.4 Factors that Affect BVOC Emissions from Plants

The BVOC emissions are regulated by biotic and abiotic factors. BVOC emissions from plants will be influenced quantitatively and qualitatively when induced to stress. Certain compounds will be emitted only upon stress. Apart from these induced emissions, the constitutive emissions will also be altered in response to stress. The emissions will also vary significantly before and after every stress. The quantity of the emissions can either increase or decrease once the plant gets acclimatised to certain conditions. For example, the composition of VOC emissions is dominated by sesquiterpenes and GLVs when plants are subjected to insect herbivory (D. F. Zhao et al., 2017; Köllner et al., 2013). Plants detect and cope with a specific stress depending on the severity and extent of that stress (Niinemets, 2009). Understanding the relationship between the characteristics of stress elements and plant BVOC emissions can give an understanding of the factors that control BVOC emissions.

Typical abiotic factors that control stress are pressure, relative humidity, temperature and light. Of these, temperature and light have been studied and related with several BVOC emissions from different environments and species. VOC emissions vary spatially and temporally and this variation is a result of the relationship between plants and environmental factors that are still unclear.

2.4.1 Temperature and Light

Temperature and photosynthetic active radiation (PAR) are the major environmental factors that affect BVOC emissions. Guenther et al. (1995) derived an empirical relation between isoprene emissions with light and temperature and a temperature-dependent relation for monoterpene emissions. The light dependence of isoprenes comes from the fact that its synthesis is dependent on products produced during

photosynthesis (Sharkey, 1996; Kesselmeier and Staudt, 1999). The synthesis and emissions occur simulatenously as isoprene is not stored and the emissions cease under dark conditions. For monoterpenes it is more complicated as these get stored in resin ducts or glands and emissions depend on temperature and resin pressure (Kesselmeier and Staudt, 1999; Rissanen et al., 2019). Almost all BVOCs have shown a dependence on temperature and studies have confirmed that the temperature-algorithm explains most of the emissions (Niinemets et al., 2004; Fitzky et al., 2019; Tarvainen et al., 2005; Grabmer et al., 2006). However, this dependency is plant species-specific and also depends on other characteristics such as plant physiology (Fitzky et al., 2019). Recently, the emissions of monoterpenes have been confirmed to be controlled also by light (Dindorf et al., 2006; Jardine et al., 2020). Certain trees like birch do not have storage sacs and therefore the emissions of monoterpenes have been confirmed to be controlled by light too (Mengesha et al., 2014; Haapanala et al., 2009). Nevertheless, the simple yet powerful relationships can be used to model emission of BVOCs effectively for short-term variations. Temperature and light alone cannot explain BVOC emissions and there are several other factors that come into effect such as the properties and characteristics of each compound, that need to be studied in detail (Filella et al., 2007).

2.4.2 Concentration of Atmospheric Gases

The rising atmospheric concentrations of ozone, carbon-dioxide and other gases can either increase or decrease the BVOC emission levels depending on duration. Elevated concentrations of carbon-dioxide could enhance photosynthesis and carbon fixation, thereby increase BVOC emissions on a short time-scale (Peñuelas and Llusià, 2003). The influence of carbon-dioxide concentrations on BVOC emissions can depend on species and environmental conditions. Possell et al. (2005) showed that when carbon-dioxide concentrations rose from 180 ppm to 366 ppm isoprene emissions decreased by 66%. Loreto, Fischbach, et al. (2001) found that while emissions

of α-pinene, sabinene and β-pinene reduced, limonene emissions increased at elevated concentrations of carbon-dioxide. But the overall monoterpene emissions were inhibited under elevated conditions of carbon-dioxide in the absence of other stress factors. Compounds other than terpenoids were observed to have increased emissions under higher carbon-dioxide concentrations (J. S. Yuan et al., 2009). Ozone is another important atmospheric gas that is likely to increase due to global warming. Higher ozone concentrations cause oxidative stress on plants (Iriti and Faoro, 2007). Since isoprene and other terpenes are important antioxidants in the plant cells, enhanced ozone will increase BVOC emissions, especially terpenoids. But not all plants respond in a similar way to ozone concentration. For example, Peñuelas et al. (1999) showed that terpene emissions from Aleppo pines were not influenced by ozone concentrations while tomatoes emitted more BVOCs with increasing ozone. To summarise, the impact of ozone on BVOC emissions depends on plant species, the compound emitted and environmental conditions.

2.4.3 Other Factors

Besides, temperature and light that drive the major fraction of BVOC emissions, there are many other factors that are not mentioned in detail in this thesis. Factors like relative humidity and soil moisture are some of the other abiotic factors that impact BVOC emissions from plants. Schade et al., 1999 observed monoterpene emissions to be dependent on humidity and proposed an emission model that incorporated both humidity and temperature. In another study, maximum amount of induced emissions from corn plants occurred between 45% and 65% relative humidity without affecting the emission composition (Gouinguené and Turlings, 2002). The same study observed that soil moisture either increased or decreased the emission rates of individual compounds while there was a decrease in the total induced emissions with increase in soil moisture.

There are also biotic factors such as induction by pathogens, insects or other

herbivores that affect the BVOC emissions greatly (Šimpraga et al., 2019). Biotic stresses account for 40% of the total stress that is experienced by almost half the population of trees in Europe (D. F. Zhao et al., 2017). The duration and extent of these biotic stresses are speculated to grow with time due to the changing climate (Faiola and Taipale, 2020). Currently, BVOC emission models do not incorporate biotic stresses as the ability to model biotic driven emissions are difficult (Peñuelas and Llusia, 2001; Faiola and Taipale, 2020). There is still lack of understanding on how all the biotic and abiotic factors would impact the BVOC emissions as it depends on a wide range of parameters. Moreover, the combined impact of both these factors create large uncertainties partly due to its complexity and partly due to lack of research. However, it is highly important to understand them so that reliable predictions can be made and the consequences of varying BVOC emissions in the ecosystem can be fully understood.

2.5 Volatile Organic Compound Emissions from Birch and Spruce Trees

Boreal forest comprises 15,000 sq. Kms. in Northern America and Eurasia. It is the largest biome in the world (Ghirardo et al., 2010). Being this large, the biome poses itself as one of the important sources of BVOCs emitted into the atmosphere (Ghirardo et al., 2010; Mengesha et al., 2014). It is one of the biomes that is low in human settlement and so the air quality in these regions will comprise very less pollutants and contain immense amount of BVOCs. The boreal forest is dominated by conifer trees like pine and spruce. In Europe, the main coniferous tree species are Pinus sylvestris L. and Picea abies L (Hakola et al., 2000; Šimpraga et al., 2019). The boreal forest also contains species like birch which are quite common but not dominant (Ghirardo et al., 2010). Conifer trees such as spruce possess storage structures called resin ducts in the leaves, wood and bark that contain terpene-rich oleoresins

(Šimpraga et al., 2019). There are complex chemical compounds found in the resin ducts of Norway spruce. Monoterpenoids and diterpenoids together make up the largest fraction of terpenoids in the stems of Norway spruce (Faldt et al., 2003). Miller et al. (2005) observed that enzyme activity and chemical accumulation in needle tissues of conifers were less compared with that in the stem. Birch also contains several compounds that have not been observed in its emission spectrum before, such as the triterpene botulin obtained from the bark of Downy birch (Keinänen et al., 1999; Abyshev et al., 2007) and other complex and non-volatile compounds from the leaves of Silver birch (Peltonen et al., 2005). However, only a few compounds have been observed irrespective of the complex chemicals present in birch and spruce. The terpenes that are widely studied from birch and spruce will be explained in the following sections.

2.5.1 Isoprene Emissions

In the European boreal territory the total BVOC emissions over the year is dominated by coniferous trees. However, during the summer months, the deciduous trees like birch make significant contributions to the isoprene emissions (Hakola et al., 2003). Birches have been regarded as low isoprene emitters, but significantly contribute to monoterpene, sesquiterpene and oxygenated BVOC emissions (Haapanala et al., 2009; Mengesha et al., 2014; Lindfors and Laurila, 2000). Norway spruce (Picea abies) is also a low isoprene emitter, but its dominance in the boreal forest and its high leaf biomass makes it an important source for isoprene (Hakola et al., 2003; Hakola et al., 2000; Lindfors and Laurila, 2000; Hakola et al., 2017). Wang et al. (2017) observed very little amount of isoprene compared to monoterpene and sesquiterpene from spruce across different seasons, while Haapanala et al. (2009) reported negligible emissions of isoprene from Mountain birch (Betula pubescens).

Table 2.2: Major BVOC Emission Potentials (at 30°C leaf temperature and 1000 µmol m^{-2} s^{-1} PPFD) of leaves (Mountain birch) and needles (Norway spruce) in µg g_{DW}^{-1} h^{-1} (Šimpraga et al., 2019)

Compounds	Emission Potentials	
	Mountain birch	Norway spruce
Isoprene	0	1
Monoterpene	3.0	2.5
Sesquiterpene	0.2	0.1

2.5.2 Monoterpene and Sesquiterpene Emissions

Norway spruce and Downy birch emit monoterpenes levels aplenty. While conifer trees like spruce contain storage resin sacs to store monoterpenes, birch trees do not contain such structures (Ghirardo et al., 2010). Hence, the emissions of monoterpenes and sesquiterpenes from birch trees should be related to the photosynthesis which depends on light and temperature (Haapanala et al., 2009; Ghirardo et al., 2010). Haapanala et al. (2009) observed almost ten times the emissions of monoterpenes to sesquiterpenes in a Mountain birch tree. It is also speculated that the considerable emissions of sesquiterpenes could be related to herbivory damage. In a study conducted in Germany, Norway spruce showed very high emissions of monoterpenes during summer, while sesquiterpenes, although not as high as monoterpenes, were maximum during early spring and reduced greatly during wet and cold season (Bourtsoukidis et al., 2014). The emission pattern from spruce was not the same in the study by Hakola et al. (2017) in Finland, where higher emissions of sesquiterpenes and monoterpenes were found in early autumn. These emissions are ten times lower than those found in the German study.

2.6 BVOC Measurement Techniques

Measuring and quantifying the plant-emitted BVOCs is important to study its impact on global climate change and the role it plays in the functioning of the ecosystem. The increasing interest in the diverse applications of plant emissions has led to numerous measurement techniques. Measurement of BVOCs can be conducted at different levels (leaf to ecosystem), with each level having its benefits and challenges. Problems occur quite often and can cause enormous uncertainties in the measurements especially when up-scaling or down-scaling a specific measurement technique (Niederbacher et al., 2015). Such obstacles make the study of plant emissions unique and challenge the scientific community to invent new measurement techniques to address several issues. Depending on the objective of the study, the required environmental parameters and observation scale, scientists have devised their own techniques that would give the least uncertainty for their observations (Niederbacher et al., 2015). This thesis will provide a review on the plant to leaf scale measurements that employ PTR-MS method to characterise and quantify BVOC emissions. PTR-MS is a widely used technique to measure VOCs in real time and in situations where fast responses to VOC emissions are required (Tholl et al., 2006; Materić, Bruhn, et al., 2015). Before providing details of the PTR-MS technique, it is important to go through the sampling methods that are used along with PTR-MS technique to observe BVOC emissions from plants.

2.6.1 Sampling Methods

Enclosure Types

Plant or leaf-scale BVOC emission studies are conducted either in laboratory-grown conditions or in the environment. The abrupt and detailed BVOC emission variations resulting from plant-ecosystem interaction which are again controlled by various factors and influences already discussed earlier can be studied intensively only

through enclosure or cuvette sampling methods. These sampling techniques allow the measurements to be conducted from the leaf-to-whole-plant level.

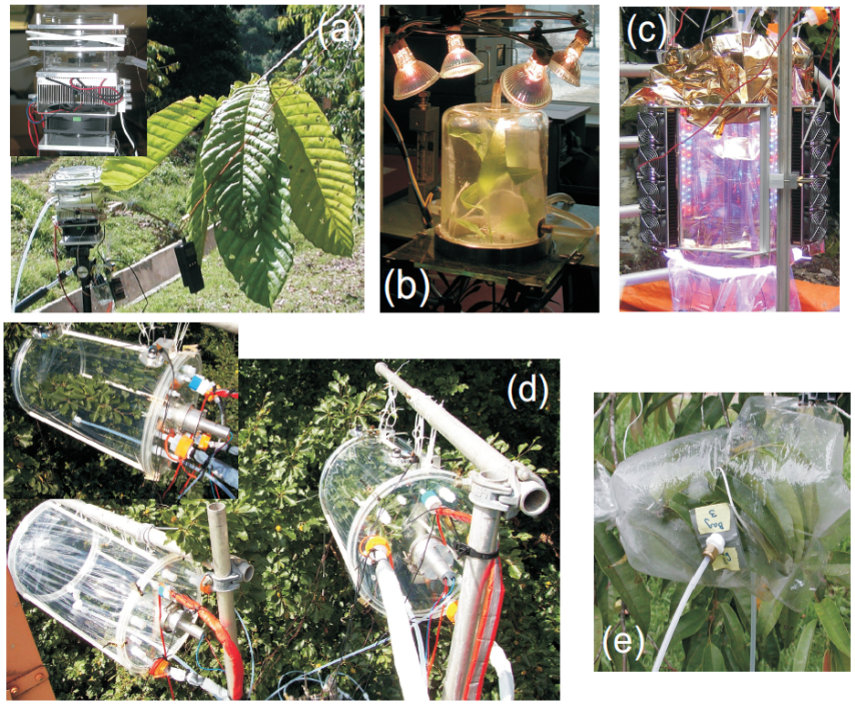

Figure 2.1: Different enclosure types used in in the field and lab observations. Glass cuvettes in the field (a) and lab (b). Teflon film branch enclosures for field measurements with artificial lighting(c) and under ambient lighting with temperature and light sensors (d). polyvinylfluoride bag for field measurements (e) (Niinemets et al., 2011).

Sampling techniques and types, varying among studies, are improved subsequently based on previous measurements and as new analytical methods are developed. In order to study the dynamics of BVOC emissions of plants, BVOC sampling might be required from the whole plant, plant parts or organs such as stem and roots. Each portion of the plant emits BVOCs in varying quantities depending on its synthesis and constitutive or induced emission. A detailed list of the different types of enclosure is given in Ortega and Helmig (2008). The enclosure consists of an inert material like Teflon, which may be wrapped around an external casing of a particular shape and size based on the type of vegetation and experiment.

Enclosure Techniques

Enclosure sampling techniques can be static or dynamic where there is absence of airflow in the static method. These enclosures may be of several shapes and sizes. In the static system, the enclosure is closed without environmental controls. Since there is no circulation of air, an artificial environment will be created within the chamber. The static enclosure technique must not be used for accurate measurements of emission rates due to the following: 1) As disturbance in vegetation causes emission bursts, there will be build-up of BVOCs in the chamber. 2)A greenhouse heating effect will be created causing elevated temperatures (above ambient) and carbon-dioxide concentrations (Ortega and Helmig, 2008; Niinemets et al., 2011). The static method opens an avenue to studying the capacity and identifying the BVOC emissions (Niinemets et al., 2011).

A more frequently used technique is the dynamic chamber method in which, complete freedom is provided to control the environmental conditions. Besides, there exists a continuous circulation of air through the closed chamber. The incoming air should be filtered (e.g. using activated charcoal) to avoid disturbance of impurities. In order to conduct several of BVOC studies such as its influence on the atmosphere, its environment response curves, and gas exchange measurements, it is important to keep the chamber environment similar to that of the ambient.

When performing BVOC emission studies, strict sampling protocols should be considered to reduce uncertainties that might arise. Some of the uncertainties (Niinemets et al., 2011; Materić, Bruhn, et al., 2015) that could arise in the quantification of emission rates are:

1. Rough handling of enclosure could lead to abrupt emissions of BVOCs. Extreme caution should be exercised when handling the chambers.

2. Appropriate use of sensors to measure environmental variables in the cham-

ber. Leaf temperature varies abruptly over the leaf surface, therefore sufficient sensors should be placed for better quantification of temperature.

3. Appropriate ratio of leaf area to chamber surface area. Appropriate chamber sizes with a medium flow rate will help in better characterisation of BVOC emissions.

4. Before measuring the emissions, duration of at least 30 minutes should be set for the emissions to reach a steady state considering chamber adjustments and plants status.

2.6.2 Proton Transfer Reaction Mass Spectrometer

The PTR-MS is a mass spectrometry technique that enables the measurement of chemicals including the most volatile organic molecules with high sensitivity and higher time response (Krechmer et al., 2018; Materić, Bruhn, et al., 2015; Tholl et al., 2006). The PTR-MS technique has been utilized to study atmospheric VOCs using aeroplanes to ground-based towers, to study BVOC emissions from plants, and in ecosystem scale flux measurements with eddy covariance methods (Taipale et al., 2008), to name a few. The advantages in using PTR-MS technique to measure plant BVOC emissions are, 1) sensitivity to detect fast real-time changes that occur in BVOC emissions (Infantino et al., 2016) and 2) low detection limits typically in parts per trillion (M. Li et al., 2019). It was in the late 1990s that the PTR-MS instrument was developed. The PTR-MS instrument works under the principle of chemical ionization technique where the molecules with proton affinities (PA) greater than H_2O undergo proton transfer reaction with the reagent ion (H_3O^+) and the product ions which are detected by the mass analyser.

$$H_3O^+ + R \longrightarrow RH^+ + H_2O \tag{2.1}$$

Kinetics of Proton Transfer reactions

In the drift tube, the reaction mentioned in equation (Eqn.)2.1 takes place. It is an exothermic reaction and takes place very quickly if PA of R is greater than PA of H_2O (J. Zhao and Zhang, 2004; Sekimoto et al., 2017). Only 1% of the H_3O^+ ions gets involved in the product ion formation (Tholl et al., 2006). The concentration of product ions will be calculated from the rate equation derived from Eqn.2.1

$$-\frac{d[H_3O^+]}{dt} = \frac{d[RH^+]}{dt} = k[H_3O^+][R] \tag{2.2}$$

The reaction rate coefficient k can be empirically derived or calculated using several theoretical models. Several studies have calculated reaction rate constants in proton transfer reactions between VOCs and H_3O^+ ions, but it is impossible to empirically derive for all compounds. Hence, theoretical models such as average dipole-orientation theory (ADO), and parameterized trajectory calculations are used to derive rate coefficient, among other models.

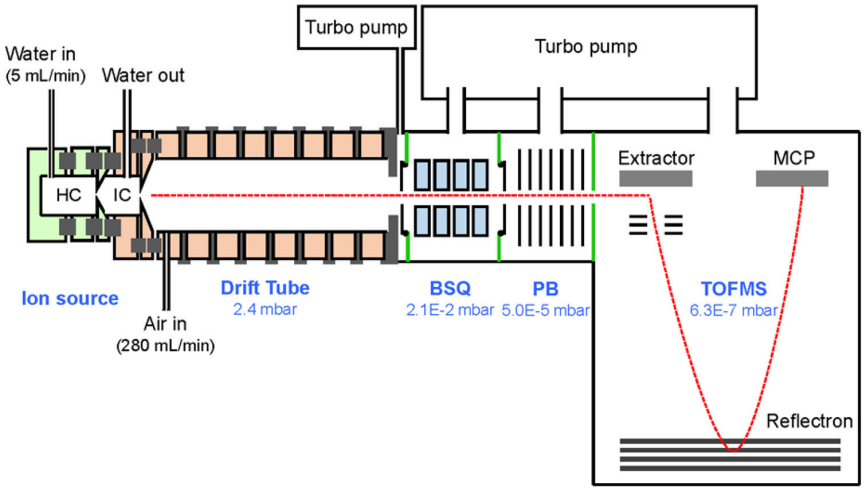

Figure 2.2: Schematic diagram of a PTR-MS with Time of Flight mass analyser. HC: Hollow Cathode Discharge. IC: intermediate chamber. BSQ: big segmented quadrupole. PB: Primary beam. MCP: Microchannel plate detector. BSQ and PB are ion regions where the ion is focussed (B. Yuan et al., 2017).

The PTR-MS instruments consists of three major regions.

1. The Ion Source

   A majority of the PTR-MS devices used today employs a hollow-cathode discharge ion source that produces H_3O^+ ions of high purity (99.5%) from pure water vapour. The reaction that takes place in the ion source to produce the H_3O^+ ions is complex with the production of fragment ions (OH^+, O^+, H_2^+, H^+) (Ellis and Mayhew, 2014). The production of fragment ions in turn takes place in complex reactions that lead to the formation of H_3O^+. In order for all these reactions to take place, a space called the source drift region is sometimes added between the drift region and discharge source. The ion sources can be of different types such as a plane electrode DC discharge source, and radioactive ion source.

2. The Drift Tube

   The ions then enter the drift tube, the major component of the PTR-MS where protonation of sample air occurs according to Eqn.2.1. A voltage is applied across the drift tube in order to generate an electric field across the tube. This electric field helps to accelerate the ions to their appropriate velocities so that it carries itself to the mass analyser. The electric field helps to collimate the ions before entering the analyser and helps to reduce water cluster formation, which hinders in accurate estimation of mass concentration. The drift tube is made up of several rings that are equally spaced and separated by insulating material to seal the vacuum in the drift tube and isolate the rings from one another. The electric field can also be produced by using resistive glass instead of rings. The sample air is ionized at the beginning of the drift tube where it is introduced through a small orifice. All molecules in the sample air with PA greater than that of water can be ionised. The advantage of using water as the reagent ion is the fact that the common components of air (N_2, O_2, CO_2) are not ionised and almost all biologically emitted volatile organic compounds

undergo chemical ionization (J. Zhao and Zhang, 2004).

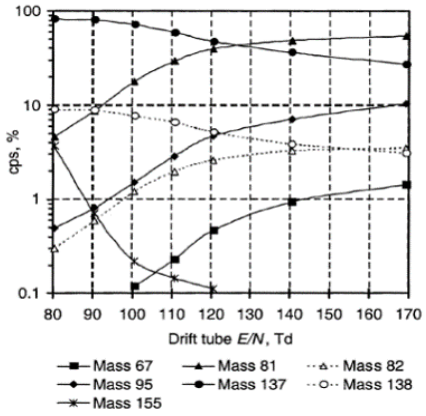

Figure 2.3: Fragementation of different ion masses is a function of drift tube E/N . While monoterpene (m/z 137) is abundant at low E/N, limonene becomes significant only at high E/N. Normal operating conditions must be opted for all PTR-MS analyses (Here, 210-130 Td. (Hewitt et al., 2003).

The ratio of electric field to the gas number density (E/N) in the drift tube is an important parameter that influences the energy of the collisions between the reagent ions and the neutral gas in the drift tube. This ratio is called the reduced electric field and has important implications in the product and reagent ion distribution in the drift tube. There is continuous collision of molecules in the drift tube which results in the breakdown of compounds into smaller molecules, a process called fragmentation and formation of water cluster ions. The E/N parameter controls this fragmentation (Fig.2.3) and water cluster formation (Hewitt et al., 2003). This parameter is controlled using temperature, pressure and electric field in the drift tube. Lower E/N results in the formation of water clusters while a high E/N creates fragmentation of the product ions, both of which are problematic for compound identification (Hewitt et al., 2003; Ellis and Mayhew, 2014). For example, Kim et al. (2009), observed lower sesquiterpene signal with increase in E/N ratio. The normal E/N working conditions are between 100-140 Td (1 Townsend (Td)= 10-17 Vcm^{-2}) (B. Yuan

et al., 2017; Hewitt et al., 2003; Ellis and Mayhew, 2014).

3. The Mass Analyser

The mass analyser is the region where the analyte molecules are detected and a mass spectrum of the ions is obtained as a function of the number of ions and mass to charge ratio (m/z). Since in a PTR-MS the m/z value is always equal to the mass of the ion, interpretation of the signal is quite simple. There is a wide range of mass analysers available today (Fig.2.4) and there are certain factors that need to be taken into consideration before choosing the analyser (Haag, 2016):

(a) The width of the m/z range to be analysed.

(b) Resolving power of the analyser.

(c) Limit of detection required.

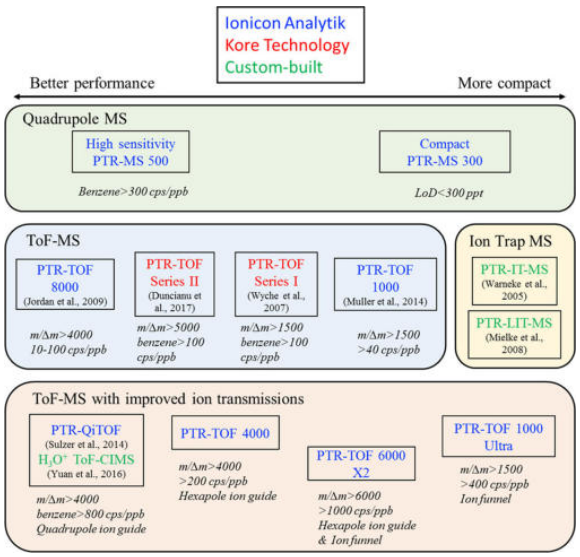

Figure 2.4: A few different PTR-MS systems with different mass analysers. Performance of the instruments comes at the cost of compactness (B. Yuan et al., 2017).

There are different mass analysers, each one being advantageous for a particular study. Nonetheless, the most commonly used analysers are quadrupole,

time-of-flight (TOF), ion-trap, Fourier transform and magnetic sector. Analysers are also used in combination with each other for better detection of compounds (Haag, 2016). The conventional PTR-MS technique involves the use of a quadrupole mass analyser, which is one of the most popular among other mass analysers.

The Time of flight mass analyser is a heightened technology in mass spectrometry that assures high mass accuracy and sensitivity and low limits of detection (Boesl, 2017; Jordan et al., 2009; Graus et al., 2010). Data acquisition for the TOF-MS was also really quick such that a single pulse produced an entire mass spectrum of a complex gas emission (Boesl, 2017). A TOF mass analyser consists of a very short accelerating region and a long field-free region that is called the flight tube.

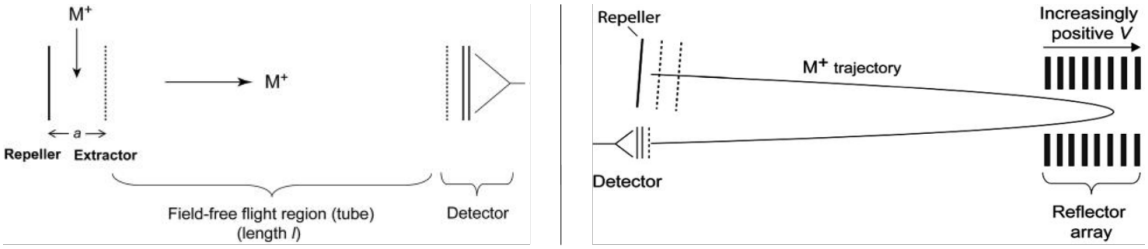

Figure 2.5: Schematic diagram of (left) linear time-of-flight mass analyser. M+ is the incoming protonated ion entering the acceleration region of the analyser. (right) A Reflectron time-of-flight analyser. (Ellis and Mayhew, 2014).

In a linear time of flight analyser (Fig.2.5, left), the collimated ions that acquire the same accelerating energy from the drift tube enter into the accelerating region of the TOF-MS in a direction that is perpendicular to their direction of propagation. Sets of electrodes in the accelerating regions, called the repeller and extractors, initially possess an equal and positive electric potential so that once the ions enter this accelerating region, their direction is slightly altered from their direction of propagation. Then the ions are pushed ahead in the perpendicular direction by a rapid increase in potential of the repeller than

the extractor. This causes the ions to accelerate into the flight tube, and an ion detector at the end records the signal as the number of ions that collide with the detector. The principle of TOF mass analyser is that when different ions are accelerated from the drift tube with same energy and allowed to drift without any interference in a field free region, their time of arrival will be different because of their molecular weight. If the potential V is applied across the electrodes in the accelerating region where ions with charge q enter from the drift tube, then the equation for kinetic energy (KE) of the molecule is,

$$KE = qV = \frac{1}{2} * mv^2 \tag{2.3}$$

$$t = \sqrt{\frac{l^2 m}{2eVz}} \tag{2.4}$$

where m is mass of ion, z is charge of the ion (q=ze), v is velocity, l is the length of drift tube which the ion travels in time t.

Therefore, the time the ion takes to travel to the detector allows the determination of the m/z value (Eqn.2.4). The TOF mass analysers are able to split isobaric ions better than quadrupole mass analysers through the application of a field-free region that allows the ions to drift towards the detector. An alternative mass analyser which employs an increased drift time in the field-free region is called the reflectron TOF mass analyser and is equipped with higher mass resolution and sensitivity (B. Yuan et al., 2017; Ellis and Mayhew, 2014; Haag, 2016) than traditional TOF analysers. The schematic sketch is seen in Fig.2.5 (right). The additional equipment is the presence of electrodes at one end of the drift region that reflects the ions in the opposite direction towards the ion detector. This electrode is called the reflector. This simple yet powerful enhancement corrects errors in the kinetic energy of the ions that

occur during propagation and leads to effective splitting of isobaric ions (Haag, 2016). To summarize, the TOF mass analysers have a wide mass range due to their transmission efficiency, and their ability to acquire the mass spectrum swiftly coupled with considerable separation of isobars gives TOF analysers the potential to measure complex real time emissions.

PTR-MS can be equipped with different mass analysers or can also be coupled with gas chromatography for analyses of isomers at low concentrations (Materić, Lanza, Sulzer, Herbig, Bruhn, Turner, et al., 2015). As there is a possibility for terpenoid emissions from plants to be small, PTR-MS techniques have considerably low limits of detection and can be used to analyse these emissions. PTR-TOF-MS techniques are widely used due to high mass resolution and time resolution of less than a second, which is perfect for real time measurements (Niederbacher et al., 2015). The technique has been employed in identifying isoprene (Brilli et al., 2011), monoterpenes (Materić et al., 2017), sesquiterpenes (Taiti et al., 2017), diterpene (Yáñez-Serrano et al., 2018) and other VOCs (Aprea et al., 2015), and studying the influence of BVOC emission from herbivory damage, abiotic stress factors in plants and is also used in above-canopy flux studies.

3. Data Collection and Analyses

3.1 Measurement Site

For this study, the BVOC emissions are measured with the Vocus proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF MS). The BVOC emissions were collected from one Betula pubescens (Downy birch) and one Picea abies (Norway spruce) trees at Hyytiälä located in southern Finland (61°50'N 24°17'E). The site is mainly a forest with a few houses and fields in surroundings. The forest is dominated by conifers, mainly Scots pine but also consists of Norway spruce. However, the forest also has a minor population of deciduous trees like birch and aspen. The emissions were collected during the month of August in 2019, which is a period of late summer in Finland. The birch tree emissions were observed for nine days that commenced on August 14, 2019 and lasted until August 23, 2019, while the spruce emissions were observed for a single day, from August 23, 2019 to August 24, 2109.

3.2 BVOC Sampling

The shoot to be observed was placed inside a closed frame chamber which was covered with a transparent Teflon enclosure. The sampling chamber also consisted of a temperature and relative humidity (RH) sensor inside it, while a PAR sensor was placed outside on one end of the chamber. The Vocus was connected to the sampling chamber with almost a 3 metre long Teflon tube. The sampling line was enclosed with a thick covering to prevent penetration of UV-rays, gas penetration and BVOC

escape. The total sample flow to the Vocus was maintained at 2.5 L/min throughout the measurement period.

3.3 Vocus Proton Transfer Reaction Time of Flight Mass Spectrometer (Vocus PTR-TOF MS)

As mentioned in section 2.6.2, a PTR-TOF-MS consists of three portions: an ion source, a drift tube and a Time of Flight Mass analyser. Traditionally, the drift tube uses an electric field in the axial direction to direct the beam into the analyser and curb cluster ion formation. Within the drift tube of any PTR-MS system, there is formation of cluster of the reagent ion, which can at most times react with VOCs, and cause misinterpretation of the mass spectrum. This cluster ion formation is also greatly dependent on the humidity of the sample air and working conditions of the instrument (Hewitt et al., 2003). Another factor that reduces detection efficiency is the long inlet for the introduction of sample air, which causes unwanted wall interactions. The Vocus is able to overcome several of these issues.

The Vocus PTR-TOF-MS is an improvement upon the traditional PTR-MS built by TOFWERK AG. The ion source and the discharge tube in the Vocus are modified for enhanced detection of compounds. The new ion source uses plasma produced in concial surface to protonate the reagent, which is different from the design of the traditional hollow cathode ion source (Krechmer et al., 2018). The pressure of the ion source is also lower than conventional PTR-MS ion sources that runs at 2.0-4.0 mbar (H. Li, Riva, et al., 2020). In this study, the pressure of the Vocus ion source was maintained at 1.4 mbar and the voltage, around 422 V. The drift tube of the Vocus called Focusing Ion-Molecule Reactor (FIMR) is made of glass with a resistive coating that enables the development of an axial electric field (around 500 V in this study) across the tube. This method was proven to be better than the stacked rings that are used to produce the field in traditional PTR-MS. The

sample air is introduced into the FIMR through a short inlet and the pressure of the FIMR is around 1.4 mbar. Only 100 sccm of sample air enters the reactor. The key difference in the Vocus is the employment of quadrupole rods placed radially on the resistive glass drift tube. These rods establish a radio frequency field that helps to enhance kinetic energy of ions and collimate the beam into the TOF mass analyser. This has proven to improve the detection of product ions (Krechmer et al., 2018). The frequency of the RF field was maintained at 1.3 MHz. The reaction chamber in the FIMR is also heated to avoid adsorption of compounds by the walls of the chamber. Krechmer et al. (2018) has given a detailed account on the dimensions and on the working of the Vocus.

From the drift tube, the protonated molecules are guided into the state of the art Long Time of Flight (LTOF) analyser, where a reflector is used to direct the ions to the detector plate. So, the ions from the FIMR are directed orthogonally towards a reflector plate and then refocused on to a plate where the ions are detected. The longer flight tube enhances the accuracy to measure the ions. The long flight tube of the Vocus PTR-TOF provides a mass resolving power of upto 15000 m/dm (H. Li, Riva, et al., 2020).

In this study, water was chosen as the reagent ion. Sample air from the chamber is pumped into the FIMR and compounds having PA greater than water (697 kJ $mol^{-}1$) will undergo protonation reaction. The protonation reaction is given in (Eqn.2.1). After protonation, the beam is guided into the time of flight mass analyser where the ions are separated depending on the velocity, which is further dependent on their respective mass-to-charge ratio (Eqn.2.4). When the ions hit the negatively charged detector plate, a current is created due to the movement of electrons and the amplitude of the current gives a measure of the number of ions striking the plate.

3.4 Calibration and Analyses

The data from the Vocus is recorded using TOFDaq Recorder provided by the manufacturer of Vocus, TOFWERK AG. The data obtained are a spectrum of measure of ion count in the y-axis as a function of m/z (m-mass, z-charge) values of the products in the x-axis. The data are processed using Tofware that provides mass calibration, baseline subtraction and molecular formula assignment to the identified ions and also time series of the data being analysed. The application runs in the Igor Pro environment (WaveMetrics, OR, USA).

The Vocus was calibrated every three hours during the measuring period using a calibration gas tank containing 16 different compounds. The calibration of the Vocus is automatically integrated with the background measurements, which is another advantage of the Vocus. The calibration factors for $C_5H_9^+$, $C_{10}H_{17}^+$ and $C_4H_7O^+$ were calculated using authentic standards. These calibration factors were used to calculate their respective concentrations. The concentrations of $C_{10}H_{15}^+$, $C_{15}H_{25}^+$ and $C_{20}H_{33}^+$ were calculated using the calibration factor of $C_{10}H_{17}^+$. The concentrations of all the oxygenated compounds were estimated using the calibration factor of $C_4H_7O^+$.

3.5 Emission Rate Calculation

The emission rate of BVOCs is defined as the mass of compounds emitted per gram from leaves and can be calculated using the following formula:

$$\mathrm{E} = \mathrm{C} * \mathrm{F}/\mathrm{m} \tag{3.1}$$

where E is the emission rate (µg g_{DW}^{-1} h^{-1}), C is the concentration of BVOC in µg m^{-3}, F is the flow of air through the branch enclosures in m^3 h^{-1}, and m is the dry weight of the leaves in g_{DW}(Hakola et al., 2001).

3.6 Emission Rate Modelling

The BVOC emissions from trees depend on various factors as stated in section 2.4. The dependency of factors such as relative humidity and soil moisture on emissions are yet to be understood clearly. But numerous algorithms have been developed to simulate BVOC emissions based on temperature and light. In this study, two different algorithms that depend on temperature and light-temperature, proposed by Guenther et al. (1993), are used to simulate BVOC emissions from birch and spruce.

3.6.1 Temperature (T)-Algorithm

The relationship of monoterpene and other BVOC emissions to temperature are usually simulated using Eqn.3.2 (Guenther et al., 1993).

$$\mathrm{E} = \mathrm{E_T} * \exp^{(\beta(\mathrm{T}-\mathrm{T_s}))} \tag{3.2}$$

where β (K^{-1}) is an empirical coefficient, T_s is the standard temperature and E_s (µg g_{DW}^{-1} h^{-1}). β describes the temperature dependency of the emission rate in Eqn.3.2. E_s is the normalized emission rate at a specific temperature (T_s=30°C), otherwise called as emission potential which accounts for the variability in the emission rates that do not result from temperature. The emission potential is also a useful variable in order to bring about comparisons with other studies.

This relationship explains short-term variations that occur due to temperature (Guenther et al., 1993). In this study, the relationship will be used to model emissions of different BVOCs observed using the Vocus and compared with the observed emissions. β values and emission potentials calculated for every compound will be used to model its respective emission rates.

3.6.2 Temperature Light (TL)-Algorithm

The second emission rate algorithm takes into account both light and temperature. This algorithm, used for modelling emissions that are directly emitted after synthesis, is strongly dependent on light and temperature. Hence, isoprene emissions are usually modelled using this algorithm given in Eqn.3.3 (Guenther et al., 1993).

$$\mathrm{E} = \mathrm{E_{TL}} * \mathrm{C_T} * \mathrm{C_L} \tag{3.3}$$

where E_{TL} is the emission rate at standard temperature and PAR, otherwise called emission potential. C_T established temperature dependency and C_L is the light dependent term.

$$\mathrm{C_T} = \frac{\exp(\frac{\mathrm{C_{T1}}*(\mathrm{T}-\mathrm{T_S})}{\mathrm{R}*\mathrm{T_S}*\mathrm{T}})}{\mathrm{C_{T3}} + \exp(\frac{\mathrm{C_{T2}}*(\mathrm{T}-\mathrm{T_M})}{\mathrm{R}*\mathrm{T_S}*\mathrm{T}})} \tag{3.4}$$

where T and T_S are measured and standard temperature (=30°C), R (=8.314 J K^{-1}) is the universal gas constant, T_M (=314 K), C_{T1} (=95000 J mol^{-1}), C_{T2} (=230000 J mol^{-1}) and C_{T3} (=1) are all empirical coefficients.

$$\mathrm{C_L} = \frac{\alpha * \mathrm{C_{L1}} * \mathrm{L}}{\sqrt{1 + \alpha^2 * \mathrm{L}^2}} \tag{3.5}$$

where L is PAR (µmol m^{-2} s^{-1}), α(=0.0027) and C_{L1} (=1.066) are empirical coefficients.

4. Results and Discussion

4.1 Environmental Variables

Environmental variables both from the chamber and ambient were recorded for the whole observation period. The temperatures in the chamber attained a maximum of 41°C and a minimum of 7°C on August 16, 2019. On three different days (August 16th, 20th and 21st) the chamber temperatures rose to 40°C. The variation in the ambient temperature was much lesser as the lowest temperature of 6°C, as observed on August 24th and it rose only up to 22°C, as observed on August 17th.

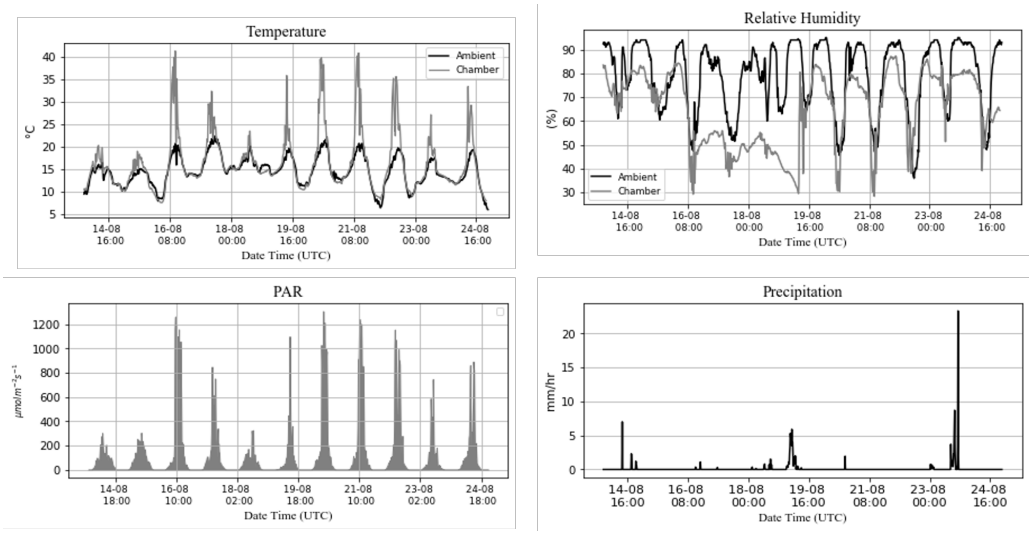

Figure 4.1: The different environmental parameters that are observed from August 14th 2019 to August 24th 2019. The black lines are ambient observations downloaded from FMI open weather data and AVAA data. The grey lines are measurements from the sampling enclosure. The ambient temperature clearly did not reach chamber temperatures, while the relative humidity in the chamber was lesser than that was observed in the ambient.

PAR reached a maximum of 1307 µmol m^{-2} s^{-1} on August 20th, 2019. PAR was considerably low on August 14th, 15th and 18th, with a maximum average of just 311 µmol m^{-2} s^{-1}. There were some cloudy days and some others with mild to very heavy rainfall during the measurement period. Lower PAR was observed on these days due to the presence of clouds and mid-day showers.

Relative humidity, along with other environmental variables, follows a clear diurnal pattern. The chamber RH is lesser than that observed in the ambient. Between August 16th and 19th, very low RH was observed in the chamber due to lack of water in the humidifier that is used to maintain the humidity in the enclosure. The eventual 40% increase in RH on August 19th is a consequence of refilling the humidifier.

A non-linear correlation was performed on temperature, PAR and RH (Fig.A.1). A strong positive correlation (r>0.8) can be found for temperature and PAR. When temperature and PAR is observed for one hour, it can be noted that temperature does not fluctuate beyond a degree when there is constant light. With a sudden increase in PAR, as observed in the morning and late in the afternoon, chamber temperature increases or decreases by a magnitude of 6°C or even higher. There is a negative relationship between temperature and relative humidity, which is expected (Fig.A.1).

Generally, the weather fluctuated throughout the measurement period. Significant noon-showers were observed on August 14th and 18th while rain was observed at night on most dates. Clear skies and a sunny weather were observed during daytime between August 20th and 22nd, and on 24th. The end of August is the late growing stage when leaves in Hyytiälä soon start changing their colour.

4.2 Terpenoid Emissions

The reported BVOC emissions are averaged for a duration of fifteen minutes. The emission rates of all compounds, as recorded on August 14^{th} and 15^{th}, are lesser than their respective mean emission rates from birch (Table A.1). Based on measurements made on August 18^{th} noon, it is found that the emission rates of the basic terpenes are closer to their respective mean emission rates from birch (Fig. 4.2). When significant emissions of terpenes are present, they are generally observed between morning and noon. Night emissions are observed but close to the detection limit of the instrument.

Downy birch and Norway spruce emitted a vast number of compounds. Of the observed terpenes, $C_{10}H_{17}^{+}$ emissions from birch has been higher than the rest. $C_{10}H_{17}^{+}$ and $C_{15}H_{25}^{+}$ reached the maximum on August 20^{th}, while $C_5H_9^{+}$ emissions reached its maximum on August 16^{th}. $C_{10}H_{15}^{+}$ emissions from birch reached only up to 0.00097 μg_{DW}^{-1} h^{-1}. *p*-Cymene ($C_{10}H_{14}$) emissions have shown to increase significantly when the tree is subjected to stress. In a study by Liu et al. (2018), when birch was subjected to stress, *p*-cymene emissions increased by a factor of 100. Other studies such as Lüpke et al. (2016) and Kari et al. (2019) have also shown similar results.

As mentioned in Lindfors and Laurila (2000) and Van Meeningen et al. (2017), birch and spruce trees are low isoprene (C_5H_8) emitters. It is evident from Fig.4.2 and Table A.1 that low emissions of $C_5H_9^{+}$ have been observed from birch. However, $C_5H_9^{+}$ emissions from spruce have contributed more than the rest of the terpenes. Due to the small data-set available for spruce, it is not possible to conclude whether the spruce observed in this study is a good isoprene emitter. Diterpene ($C_{20}H_{33}^{+}$) emissions from both the trees were observed but in lower quantities. Emissions of $C_{20}H_{33}^{+}$ from birch and spruce have not been reported in any study before. The emission pattern observed for $C_{20}H_{33}^{+}$ is such that considerable night time emissions are

realised. Yáñez-Serrano et al. (2018) reveal night time emissions of diterpenes from Mediterranean Cistaceae shurbs. Also, Matsunaga et al. (2011) show a comparable diterpene emissions to the total monoterpene emissions from conifer trees.

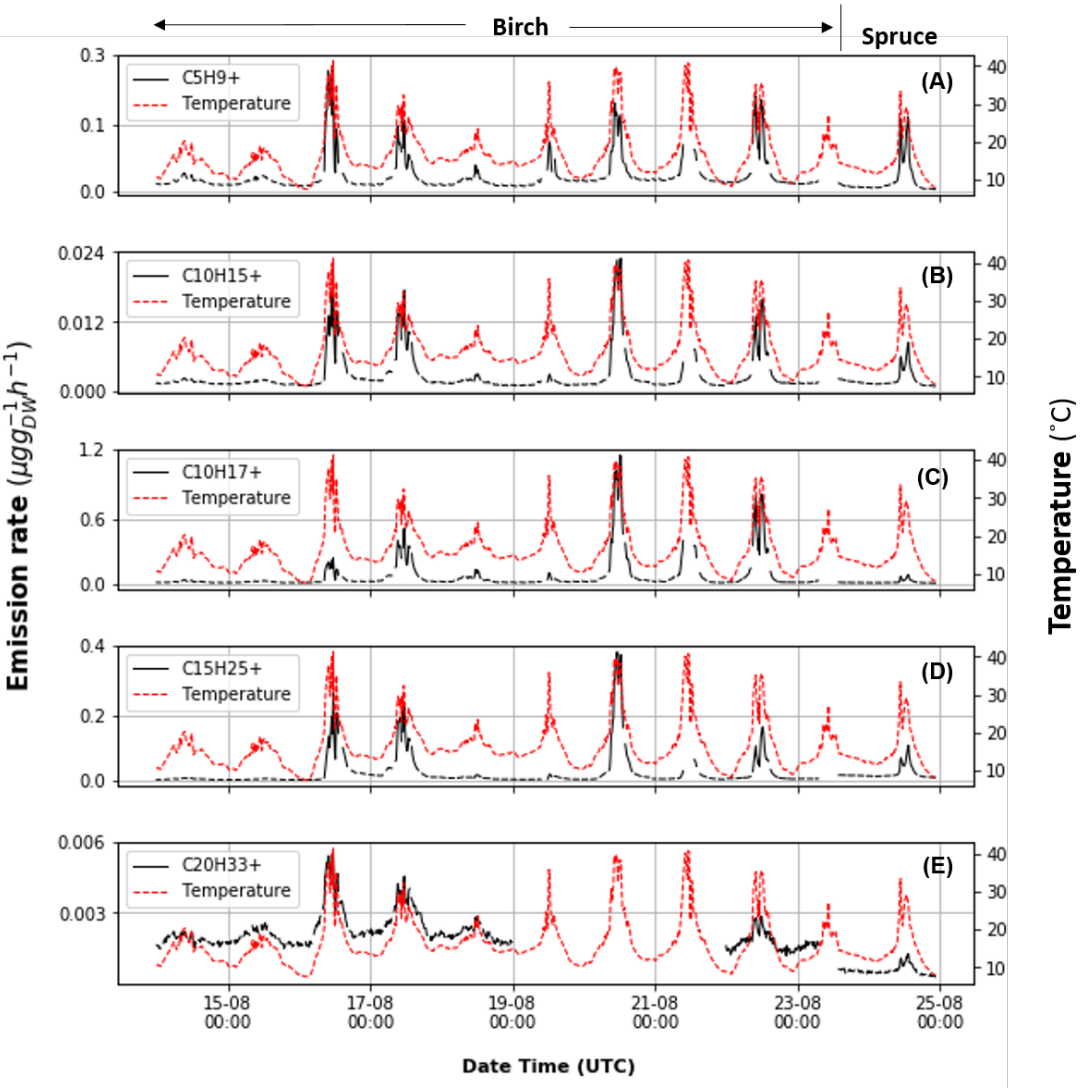

Figure 4.2: The emission rate (µg g_{DW}^{-1} h^{-1}) patterns of the major terpenoids ((A)$C_5H_9^+$ (isoprene signal), (B) $C_{10}H_{15}^+$ (*p*-Cymene signal), (C) $C_{10}H_{17}^+$ (monoterpene signal), (D) $C_{15}H_{25}^+$ (sesquiterpene signal), (E) $C_{20}H_{33}^+$ (diterpene signal)) observed between August 14, 2019 and August 24, 2019. After 13:15 on August 23, emissions were observed from spruce tree

From the emission pattern, an overall increase of emission from birch tree was observed from August 20, 2019. This is the resultant of the fact that both temperature and PAR have been constantly well above the average since August 20th. How-

Table 4.1: Linear Correlation(r) of terpene emissions rates between from birch/spruce.

	$\mathbf{C_5H_9^+}$	$\mathbf{C_{10}H_{15}^+}$	$\mathbf{C_{10}H_{17}^+}$	$\mathbf{C_{15}H_{25}^+}$
$\mathbf{C_{10}H_{15}^+}$	0.88/0.96			
$\mathbf{C_{10}H_{17}^+}$	0.76/0.97	0.90/0.98		
$\mathbf{C_{15}H_{25}^+}$	0.76/0.95	**0.97/0.99**		
$\mathbf{C_{20}H_{33}^+}$	0.77/0.92	0.8/0.96	0.47/0.92	0.81/0.94

ever, precipitation was recorded as below par from August 20$^{\text{th}}$ until the end of birch measurement period (Fig.4.1). Besides precipitation, unusually large temperatures observed on 16$^{\text{th}}$ and on 20$^{\text{th}}$ caused the emissions of terpenes in larger quantities. For example, it can be seen in Fig.4.2 that isoprene emissions peaked on 16$^{\text{th}}$ when temperature reached around 40 °C, while monoterpene emissions peaked on August 20$^{\text{th}}$. High temperature events such as these are rarely observed in Hyytiälä and these events have positive effects on the emissions of BVOCs. The weather showed an influence on emission patterns from both the trees over the short term, although the specifics cannot be determined in this study.

For birch, $C_{10}H_{15}^+$ emission rate pattern correlates well with $C_{15}H_{25}^+$ and $C_{10}H_{17}^+$, having an r value of 0.9 and 0.97 respectively. $C_{20}H_{33}^+$ and $C_{10}H_{17}^+$ emissions from birch showed the least correlation with r<0.5. $C_{10}H_{17}^+$ and $C_{15}H_{25}^+$ also correlate well (r=0.8) for birch. From Fig.4.2 and correlation coefficients, it can be inferred that the emission patterns of $C_{10}H_{15}^+$, $C_{10}H_{17}^+$ and $C_{15}H_{25}^+$ from birch tree are very similar to each other.

4.3 The Correlation of Observed Environmental Conditions on Emissions

The chamber temperature and PAR dependency can be seen from Fig.A.1. Compounds observed from both birch and spruce exhibit a strong correlation (r>0.7)

with light and temperature (Table 4.2).

Table 4.2: Linear Correlatiom(r) between terpene emission rates and chamber parameters from birch/spruce trees

Compounds	**Temperature**	**PAR**
$\mathbf{C_5H_9^+}$	0.89/0.92	0.91/0.88
$\mathbf{C_{10}H_{15}^+}$	0.87/0.89	0.80/79
$\mathbf{C_{10}H_{17}^+}$	0.80/0.86	0.75/0.79
$\mathbf{C_{15}H_{25}^+}$	0.80/0.87	0.72/0.76
$\mathbf{C_{20}H_{33}^+}$	0.83/0.92	0.70/0.77

Usually, short measurement campaigns conducted in the field tend to produce similar dependencies for both temperature and light, which makes it hard to isolate their effects (Ghirardo et al., 2010). Likewise, for $C_{10}H_{15}^+$, $C_{10}H_{17}^+$ and $C_{15}H_{25}^+$ and $C_5H_9^+$ notified in this thesis, the differences between the correlation of emission rates-PAR and emissions rate-temperature are not significant for both the trees. However, for all compounds except $C_5H_9^+$, the emission rates from both trees are slightly more correlated to temperature. $C_5H_9^+$ emissions from birch as well as spruce reflect the highest temperature and PAR correlation.

Compounds such as monoterpenes and sesquiterpenes that are conventionally treated to be solely temperature-driven can also possibly be highly correlated with light intensity. Ghirardo et al. (2010) proved that around 98-100% of monoterpene emissions from Silver birch are a function of both temperature and light. Monoterpene emissions from birch, as observed in Hakola et al. (2001), are more light dependent than sesquiterpenes, wherein the monoterpene emissions decrease upon darkening of the sampling chamber. For sesquiterpenes, most literature have supported stronger correlation with temperature than with light (Duhl et al., 2008). However, studies conducted in the lab, although they were neither on birch nor spruce,

have shown β-caryophyllene to be positively correlated with light (Gouinguené and Turlings, 2002; Hansen and Seufert, 2003) while other sesquiterpenes were either negatively correlated or were not affected by light intensity (Gouinguené and Turlings, 2002). Diterpene emissions from conifers reported by Matsunaga et al. (2011) is temperature dependent but speculated the influence of light too. The temperature and light dependency to the emission rates of these compounds is discussed in detail later in the thesis.

This study does not ascertain how relative humidity and precipitation affects BVOC emissions directly. Lower than average emission is recorded along with moderate showers as per the observations made on August 14^{th} and August 18^{th}. As per August 15^{th}, the low emissions are attributed to the reduced PAR. Even on August 14^{th}, the lower emissions from birch tree can be attributed to the reduced PAR and temperature observed during the rainy weather. A study by Vallat et al. (2005) reported increased emissions of β-caryophyllene, limonene and (E,E)-α-farnesene at high temperature and low relative humidity. In the same study, β-pinene positively correlated with both temperature and relative humidity in the night and with rainfall and temperature in the afternoon. While in an experiment conducted by Llusià and Peñuelas (2000), the total monoterpene emissions was positively correlated with relative humidity only at 15°C. Hence, it can be concluded that, it is a combination of all these abiotic factors and may possibly be due to other factors such as enzyme activity, leaf development, drought exposure that contribute to the emission controls of terpenes.

In Fig.4.3 the terpene emission rates are summed up and displayed for two different periods. The mean morning chamber temperature and PAR are found to be higher than average mid-day chamber temperatures during birch measurement period. On August 24^{th}, while chamber temperature was more in the afternoon PAR was similar for both periods. Besides 22^{nd} August, all the terpene emission rates

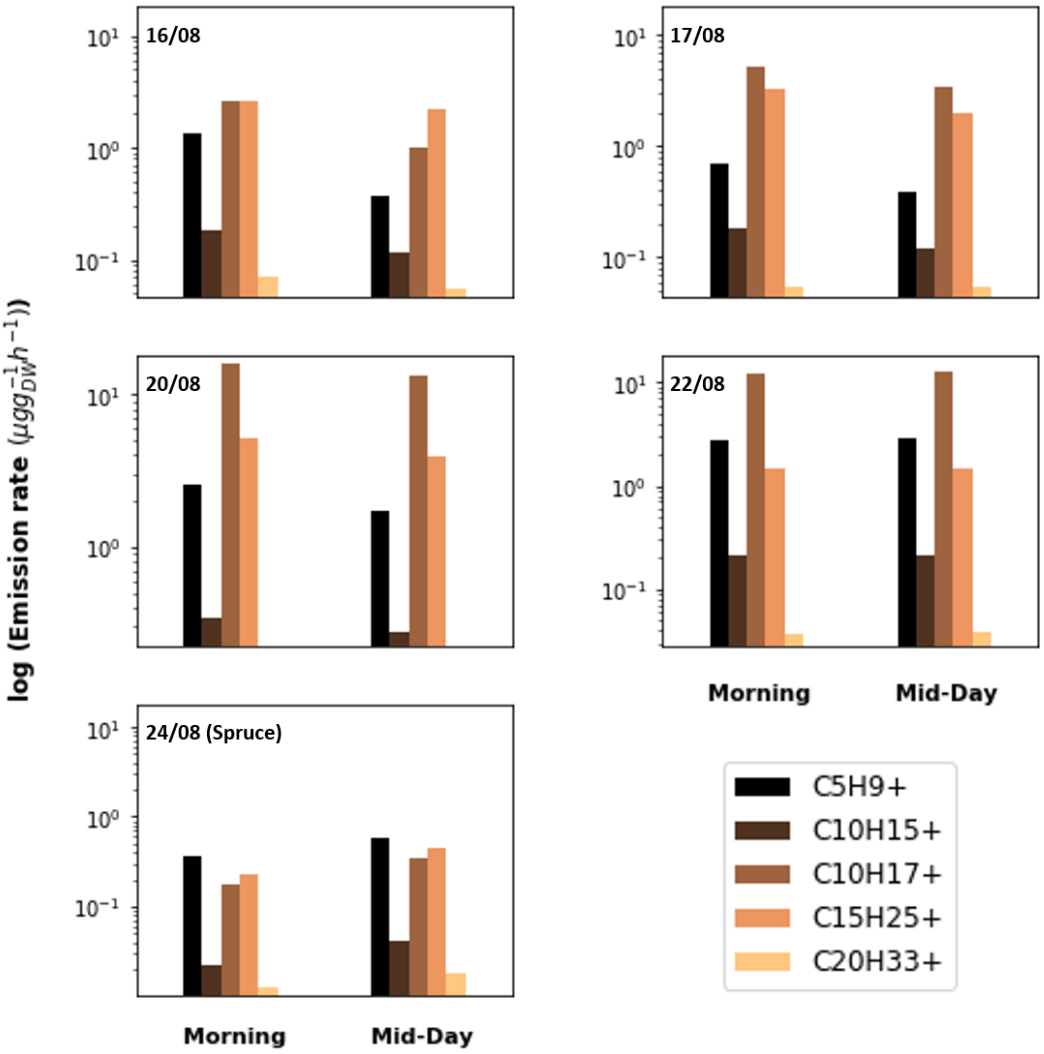

Figure 4.3: Emissions of terpenes in the morning (0830-1145 h) and mid-day (1200-1600 h) on dates when above average emission rates are measured.

from birch is higher in the morning than mid-day. On all these days except August 16th, $C_{10}H_{17}^{+}$, emission rates are the highest from birch for both time periods. Among the five observed terpenes, emission rates of $C_{10}H_{17}^{+}$ from birch is highest on August 20th and August 22nd. As per observations of August 16th, $C_{15}H_{25}^{+}$, emissions are higher than $C_{10}H_{17}^{+}$ during mid-day while almost equal amount of both are emitted as per August 16th morning. $C_{20}H_{33}^{+}$ emissions observed from birch during both the periods, are two orders of magnitude lesser than $C_{15}H_{25}^{+}$ emissions. Yáñez-Serrano et al. (2018) obtained comparable emissions of diterpenes with other terpenes in a

controlled environment while emissions observed in the field were much less when compared with those of other compounds. The study also mentioned that the reduced estimation could be attributed to the losses occurred due to ozonolysis and adsorption of diterpene onto tubing surfaces. In this thesis, the possibility of ozonolysis reaction can be eliminated as the air through the enclosure was filtered, though the latter is still possible. The $C_5H_9^+$ emissions from spruce are found to dominate as per the August 24th, followed by $C_{15}H_{25}^+$, with every compound being emitted more during the second period. It is also discerned that the mean mid-day chamber temperature is higher than morning by 2°C as per the observations made on August 24th.

From the above analyses it is inferred that for birch both mean chamber temperatures and mean PAR have positively influenced the emissions of compounds. But on August 24th, although PAR was similar during both periods, higher temperature during mid-day has influenced the BVOC emissions. This observation can also be attributed to the fact that resin structures that store terpenes in spruce are known to be controlled by temperature, while birch do not possess such storage structures. Although this hypothesis can be speculated here, it cannot be concluded due to the lack of data for spruce.

4.4 Emission Potentials

Emission potentials are calculated for the terpenes using temperature algorithm (T-algorithm) mentioned in section 3.6.1. E_T and β were derived by fitting a linear regression curve to the measured log of emission rates and the difference between temperature and standard temperature. Emissions of several terpenes can also be described by the temperature-light algorithm (TL-algorithm) mentioned in section 3.6.2. Unlike spruce, terpene emissions from birch are spontaneous due to the absence of storage structures (Rinne et al., 2009; Ghirardo et al., 2010). As mentioned earlier, since studies have found light dependency to monoterpene emissions, emissions for

birch tree is also modelled using TL-algorithm, which is normally, used for isoprene emission modelling. In order to calculate E_{TL}, C_L and C_T calculation for every measured value of PAR and temperature was performed initially. By performing linear-regression analyses on measured emission rates with product of C_L and C_T, emission potential E_{TL} for different compounds was obtained.

A significant amount of terpenes is emitted through de-novo synthesis which depends on both light and temperature even from spruce trees (Schürmann et al., 1993). Using TL-algorithm for spruce emissions yielded R^2 smaller than 0.2 and so is excluded in this thesis. The calculated emission potentials are shown in Table 4.3 for both trees.

Birch

The emission potential of $C_{10}H_{17}^+$, during the late growing season, is an order of magnitude greater than $C_{15}H_{25}^+$ for birch when calculated using T-algorithm. Similar emission potentials are obtained for $C_5H_9^+$ and $C_{15}H_{25}^+$ using both algorithms. For birch, the emission potential calculated using TL-algorithm for $C_{15}H_{25}^+$ is about 44% greater, while for $C_{10}H_{17}^+$ it is 35% greater than its respective emission potentials calculated using T-algorithm. For $C_{10}H_{15}^+$ and $C_5H_9^+$, E_{TL} values are almost 25% greater than the E_T values.

Monoterpene ($C_{10}H_{17}^+$) emission potentials from birch fall within the range of other experimental values calculated from birch tree emissions (Hakola et al., 2001).$C_{15}H_{25}^+$ emission potentials calculated using both algorithms are much lesser than obtained by Hakola et al. (2001) where the range varies between 0.3 and 6.95 µg g_{DW}^{-1} h^{-1}. Late growing season may explain the low emissions of sesquiterpenes. Also, in a study by Haapanala et al. (2009), the emission potentials calculated for monoterpenes and sesquiterpenes from Mountain birch during late summer are higher than those measured in this thesis. The emission potential of isoprene ($C_5H_9^+$) men-

Table 4.3: Emission potentials (µg g_{DW}^{-1} h^{-1}) of terpenoids from birch and spruce at standard temperature and light conditions using the temperature dependent (E_T), temperature and light dependent (E_{TL}) algorithms. β is an empirical coefficient in K^{-1}

	T-Algorithm			**TL-Algorithm**	
	β	**E_T**	**R^2**	**E_{TL}**	**R^2**
Birch					
$C_5H_9^+$	0.09	0.083	0.84	0.1	0.63
$C_{10}H_{15}^+$	0.10	0.008	0.81	0.01	0.58
$C_{10}H_{17}^+$	0.17	0.29	0.79	0.39	0.64
$C_{15}H_{25}^+$	0.17	0.083	0.69	0.12	0.63
$C_{20}H_{33}^+$	0.04	0.004	0.69		
Spruce					
$C_5H_9^+$	0.16	0.14	0.95		
$C_{10}H_{15}^+$	0.09	0.007	0.87		
$C_{10}H_{17}^+$	0.11	0.057	0.87		
$C_{15}H_{25}^+$	0.1	0.074	0.87		
$C_{20}H_{33}^+$	0.04	0.001	0.84		

tioned in Lindfors and Laurila (2000) is 0.1 µg g_{DW}^{-1} h^{-1} for Downy birch and Silver birch and it is similar to the values calculated in this thesis using both algorithms (T-Algorithm: 0.09 µg g_{DW}^{-1} h^{-1}, TL-Algorithm: 0.1 µg g_{DW}^{-1} h^{-1}). Emission potentials of isoprene from Downy birch and Silver birch mentioned in one study is 0 µg g_{DW}^{-1} h^{-1} (Šimpraga et al., 2019). Other deciduous trees like European aspen have high isoprene emission potentials, close to 60 µg g_{DW}^{-1} h^{-1} (Šimpraga et al., 2019). The values also substantiate the fact that birch is a low isoprene emitter (Ghirardo et al., 2010, Haapanala et al., 2009).

The lowest emission potential was obtained for $C_{20}H_{33}^+$. The emission potential

for diterpene is reported using T-Algorithm, as the R^2 for TL-algorithm was lesser than 0.2. The observation of Matsunaga et al. (2011) reflects diterpene emission potentials to be an order of magnitude greater than that of total monoterpenes from C.japonica and C.obtusa trees.

Spruce

The emission potential obtained for $C_{10}H_{17}^{+}$ from Norway spruce using T-algorithm is lesser to what is observed by others. In a recent study, sum emission potential of different monoterpenes from spruce observed by Hakola et al. (2017) was 0.112 µg g_{DW}^{-1} h^{-1} during late summer. Meanwhile, Šimpraga et al. (2019) mentions a value of 2.5 µg g_{DW}^{-1} h^{-1} which is much higher than obtained in the study by Hakola et al. (2017) as well as in this study. $C_{15}H_{25}^{+}$ emission potential calculated in this thesis is comparable to those mentioned in Duhl et al. (2008) wherein the emission potentials mentioned vary between 0.02 and 2.6 µg g_{DW}^{-1} h^{-1}. In Hakola et al. (2017), sesquiterpene emission potential was calculated to be 0.155 µg g_{DW}^{-1} h^{-1} during late summer. Moreover, in this study, the emission potential of $C_{15}H_{25}^{+}$ is slightly higher than that of $C_{10}H_{17}^{+}$. In a study by Hakola et al. (2017), observations conducted during different periods of summer, showed that a higher emission potential for sesquiterpenes was obtained only during late summer.

Emission potentials of isoprene from Norway spruce measured in Hyytiälä in two different studies are 0.06 and 0.1-1.2 µg g_{DW}^{-1} h^{-1} (Hakola et al., 2017, Hakola et al., 2003). Recently, a value of 0.056 µg g_{DW}^{-1} h^{-1} was obtained for isoprene emission potential from Norway spruce during late summer (Hakola et al., 2017). $C_5H_9^{+}$ emission potential obtained in this study for Norway spruce lies within the range calculated in different field experiments at Hyytiälä. $C_{20}H_{33}^{+}$ emission potential calculated in this thesis is the lowest for spruce, lesser than $C_{20}H_{33}^{+}$ obtained for birch tree.

β-*values*

The β values calculated for $C_{10}H_{17}^+$ emission from spruce are comparable to that observed by Hakola et al. (2017), where the β range for different monoterpenes vary between 0.06 and 0.19. For $C_{15}H_{25}^+$, the β value of 0.1 lies within the range of the values summarised in Duhl et al. (2008). Emission studies of Bourtsoukidis et al. (2013) that involved Norway spruce obtained β values 0.1 and 0.13 for monoterpene and sesquiterpene respectively, which are comparable to the values observed in this thesis. The β value of $C_{10}H_{17}^+$ emission from birch is close to the literature value (0.15; (Hakola et al., 2001)). For $C_{15}H_{25}^+$, the calculated β value lies in the range 0.14-0.22 (Hakola et al., 2001) and within the range 0.15-0.24 mentioned in Haapanala et al. (2009). Hence, the values of β calculated in our study for both $C_{10}H_{17}^+$ and $C_{15}H_{25}^+$ from both trees are reasonable and comparable to the ones obtained in several experiments. For both spruce and birch, the β values obtained for $C_{20}H_{33}^+$ in this study are less compared to that obtained by Matsunaga et al. (2011). In the same study, $C_{20}H_{33}^+$ showed that it was more strongly dependent on temperature than monoterpene.

4.5 Modelled and Measured Emissions

In order to understand the variation of emission models with measured emissions, both the emissions from birch were plotted for comparison (Fig.4.4). $C_5H_9^+$ emissions modelled using both algorithms obtained high R^2 values (T-algorithm: 0.88; TL-algorithm: 0.8). The 1:1 line for T-algorithm for $C_5H_9^+$ emissions is remarkably good, especially at higher emissions. Although isoprene emissions are expected to be better modelled using the TL-algorithm, it is not the case. A slightly lesser R^2 is obtained between measured and modelled emissions using the TL-algorithm due to the underestimation of modelled emissions. The difference between measured and modelled emissions is large up to a PAR value of 600 µmol m^{-2} s^{-1}. For $C_{10}H_{17}^+$

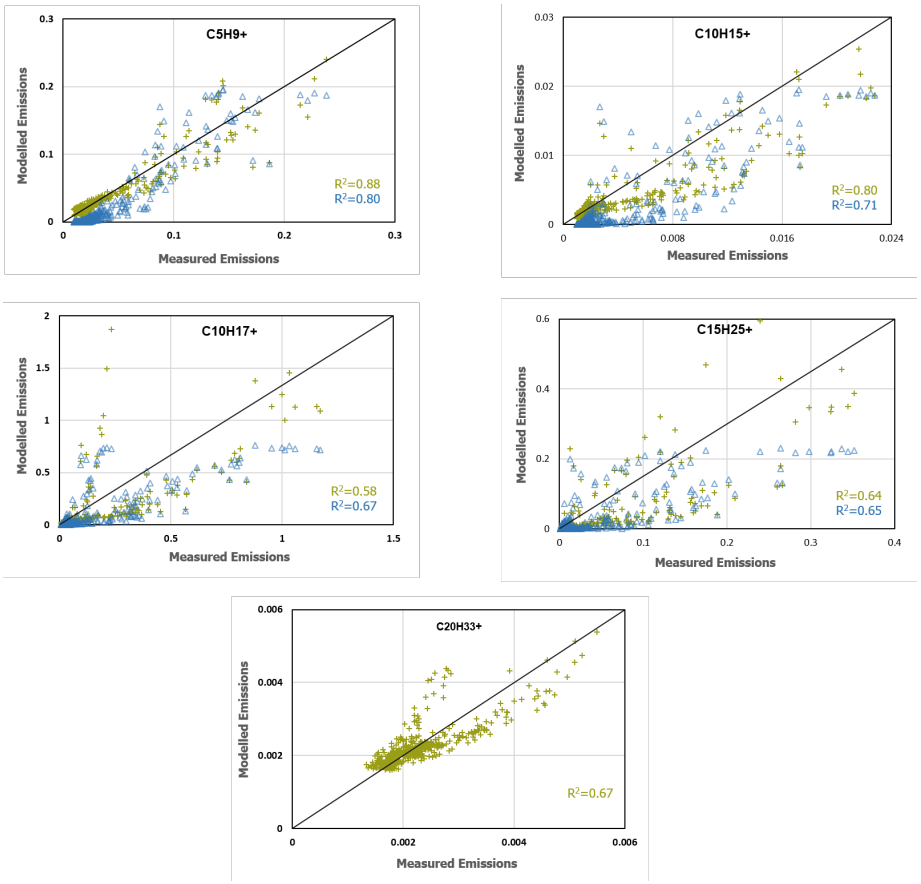

Figure 4.4: The modelled emissions of different compounds plotted against its respective measured emissions from birch tree. (+) Temperature Algorithm (T). (△) Temperature Light Algorithm (TL).

and $C_{15}H_{25}^+$, the modelled and measured emissions are highly scattered using both algorithms. $C_{10}H_{17}^+$ emissions modelled using the TL-algorithm follows the 1:1 line better and it can be speculated that light plays a role in the emissions of $C_{10}H_{17}^+$ from birch tree, as shown by Ghirardo et al. (2010). The R^2 value obtained for $C_{15}H_{25}^+$ emissions modelled using both algorithms are quite similar. Sesquiterpene emissions are known to be controlled by temperature although the effect of light has been proven (Duhl et al., 2008). In this thesis, as both models produced similar R^2, it is difficult to conclude whether light or temperature had a better influence on $C_{15}H_{25}^+$ emissions. The inability to establish this dependency on sesquiterpene emissions is also mentioned by Helmig et al. (2006). $C_{10}H_{15}^+$ modelling using T-algorithm

produced a higher R^2. However, the modelled emissions using both algorithms for $C_{10}H_{15}^+$ overestimates emission rates by a factor of 10. $C_{20}H_{33}^+$ emissions were modelled using only T-algorithm and a positive R^2 is also seen between modelled and measured emission rates. Yáñez-Serrano et al. (2018) provided substantial evidence to conclude that kaurene emissions from H.halimifolium and C.ladanifer were temperature driven (released from storage pools). Matsunaga et al. (2011) also concludes that diterpene emissions from C.japonica and C.obtusa are effectively controlled by temperature, although they speculated the role of light.

The terpene emissions cannot be explained by PAR and temperature alone even though these variables explain the variability of almost half the emissions. More environmental variables like relative humidity must be intensively studied as to how constitutive and stored emissions of trees are influenced, on both long and short term bases. For example, as observed in Lüpke et al. (2017), low soil water content can lead to a decline in overall BVOC emissions from Scots pine trees.

4.6 Oxygenated Compounds

Several oxygenated molecules having one and two oxygen atoms were identified by the Vocus. A few of them belong to known terpenoid groups. As they display an emission pattern that is not similar to the terpene molecules ($C_5H_9^+$, $C_{10}H_{15}^+$, $C_{10}H_{17}^+$, $C_{20}H_{33}^+$), the oxygenated compounds can be speculated to have different emission mechanisms and also be influenced by other abiotic or biotic factors. Thirteen oxygenated compounds are presented in Fig.A.4. Among them, two are products derived from isoprene oxidation, five from monoterpenes and three from sesquiterpenes, while the source of three others seem to be unknown.

Recently, oxidation products of isoprene have been detected to be emitted from mango branches in a study by Jardine et al. (2013). It was found in a study by Jardine et al. (2011) that the isoprene oxidation products MVK and MAC ($C_4H_7O^+$)

are formed by the oxidation of isoprene in the leaves. In this study, direct emissions of $C_5H_7O^+$ and $C_4H_7O^+$ are detected by the Vocus from both birch and spruce trees.

The signal $C_{10}H_{19}O^+$ can be a monoterpenoid alcohol (like linalool, borneol) or even monoterpenoid ether (like 1,8-cineol), which is emitted by a wide array of plants. These monoterpenoids have been reported to be emitted from Norway spruce (Hakola et al., 2017) and Downy birch (Hakola et al., 2001). $C_{10}H_{19}O^+$ was found to increase 100 times after Norway spruce foliage was treated with terpene inducing chemical to replicate physical damage (D. M. Martin et al., 2003). In this thesis, $C_{10}H_{19}O^+$ constituted 1% of observed terpenoid emissions from birch, while it is slighly above 1% from spruce. $C_{10}H_{15}O^+$, $C_{10}H_{21}O^+$, $C_{10}H_{17}O_2^+$ and $C_{10}H_{15}O_2^+$ are another set of oxygenated compounds that are detected from both trees. $C_{10}H_{21}O^+$ can either be an oxygenated monoterpene or decanal. Significant emissions of straight chain aldehydes, including decanal, have also been observed in Norway spruce emissions (Hakola et al., 2017). The emission pattern of $C_{10}H_{21}O^+$ and $C_{10}H_{15}O^+$ are entirely different from that of other compounds observed in this study. $C_{10}H_{17}O_2^+$ was reported to be emitted by Norway spruce in a study by Bourtsoukidis et al. (2013).

Oxygenated sesquiterpene compounds are very difficult to detect because of their low volatility. At a mass number of 220, several isomers of oxygenated sesquiterpenes are identified by the Gas Chromatography-MS operated by the Air Quality Group at Finnish Meteorological Institute that simultaneously measured emissions from these two trees. The compound corresponding to the same mass (m/z 221) is identified by the Vocus, having the molecular formula $C_{15}H_{25}O^+$. A compound with the formula $C_{15}H_{23}O^+$ (m/z 219) is also identified in the spectrum. Isomers of $C_{15}H_{27}O^+$ have been identified by Helmig et al. (2007) to be emitted by various pine trees in the US. Q.-H. Zhang et al. (1999) observed several oxygenated sesquiterpenes emitted from Downy birch. Among them, $C_{15}H_{25}O^+$ is also observed to be emitted in large quantities during the month of August. A very recent study done

by Isidorov et al. (2019) showed emissions from buds of Silver and Downy birch. A total of 156 compounds were detected from buds of Downy birch alone. It comprised several sesquiterpenoids and monoterpenoids containing a maximum of two oxygen atoms. Some isomers of $C_{15}H_{22}O^+$ were found to be emitted only from Downy birch, hence making it species-specific. Generally, reports of oxygenated sesquiterpenes being directly emitted from plants are fewer.

Other oxygenated compounds having the chemical formula $C_{14}H_{23}O_2^+$, $C_{11}H_{17}O^+$ and $C_{14}H_{21}O_2^+$ are observed in this thesis but could not be assigned to any group of compounds. No compound corresponding to these formulae, has been reported in the literature on BVOC emissions from plants.

Diurnal Variations of Oxygenated Compounds

For the oxygenated compounds released from the birch tree, the highest emission rates occurred right before noon. Considerable emissions are present between 8:00 and 15:OO. The oxygenated compounds exhibit a clear diurnal pattern, with the maximum occurring at 10:00 and 11:00 for different compounds (Fig.4.5). Thereafter, the emissions steadily decreased and reached early morning values. For compounds $C_4H_7O^+$, $C_{10}H_{21}O^+$, $C_{10}H_{15}O^+$ and $C_{14}H_{21}O_2^+$, the maxima for mean and median values are different. The maxima for median of $C_{10}H_{21}O^+$ occurs three hours after the maxima of its mean. A strong diurnal variation is observed in the short term observation of all oxygenated compounds. Although PAR reached zero during night, the emissions of none of these compounds is nil during the night. Correlation of emission rates of oxygenated compounds-temperature and emission rates of oxygenated compounds-PAR are very similar and hence it is not possible to conclude from this basic study whether these compounds are more dependent on temperature.

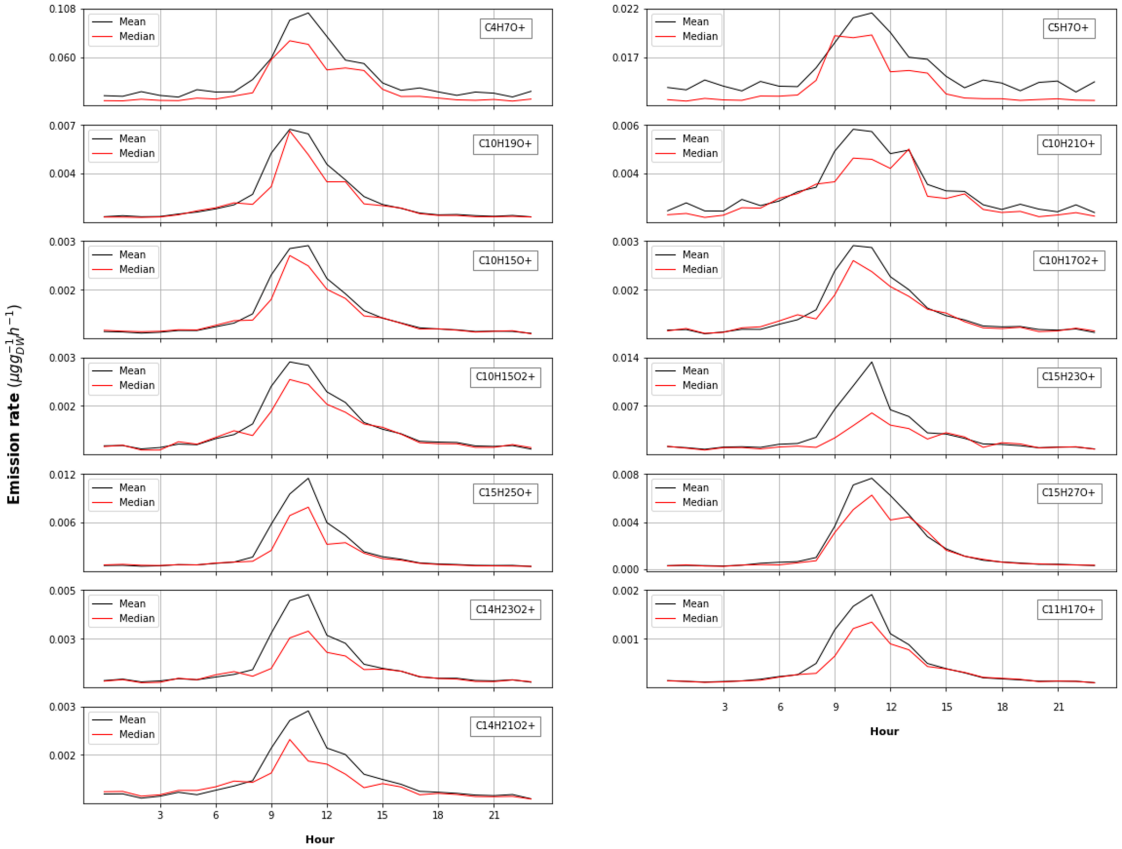

Figure 4.5: Diurnal variation of oxygenated compounds observed from birch tree.

4.7 Contribution of BVOCs Observed from Birch and Spruce Trees

Wide varieties of compounds are observed from both birch and spruce with products of terpenes and also several oxygenated compounds being emitted. $C_{10}H_{17}^{+}$ accounted for 39% of the emission from birch over the whole measurement period. The high emissions of $C_{10}H_{17}^{+}$ are observed from 10:00 to 12:00 (Fig.4.7). Although $C_{10}H_{17}^{+}$ emissions are almost the same for a couple of hours, the sum emissions of all the observed compounds peaked at 11:00. $C_5H_9^{+}$ is known to peak during central hours of the day due to its dependency on light and temperature. In this study, $C_5H_9^{+}$ has been found to peak around the same time. From birch, $C_5H_9^{+}$ emissions peak at 10:00 and from spruce, these emissions peak at 13:00.

4.7. CONTRIBUTION OF BVOCS OBSERVED FROM BIRCH AND SPRUCE TREES

$C_4H_7O^+$ was emitted as much as $C_5H_9^+$ from birch, which is a major product of $C_5H_9^+$ in the atmosphere. As mentioned earlier, $C_4H_7O^+$ exhibits a clear diurnal cycle with a peak at 11:00. Hyytiälä is also a region where there is constant and considerable presence of $C_4H_7O^+$ in the atmosphere (Patokoski et al., 2014). Isoprene oxidation products are usually emitted in low quantities and are masked by high emissions of isoprene (Jardine et al., 2011). But in this study $C_4H_7O^+$ is seen to contribute more than $C_5H_9^+$ from birch, while it was found to have lesser contribution than $C_5H_9^+$ from spruce.

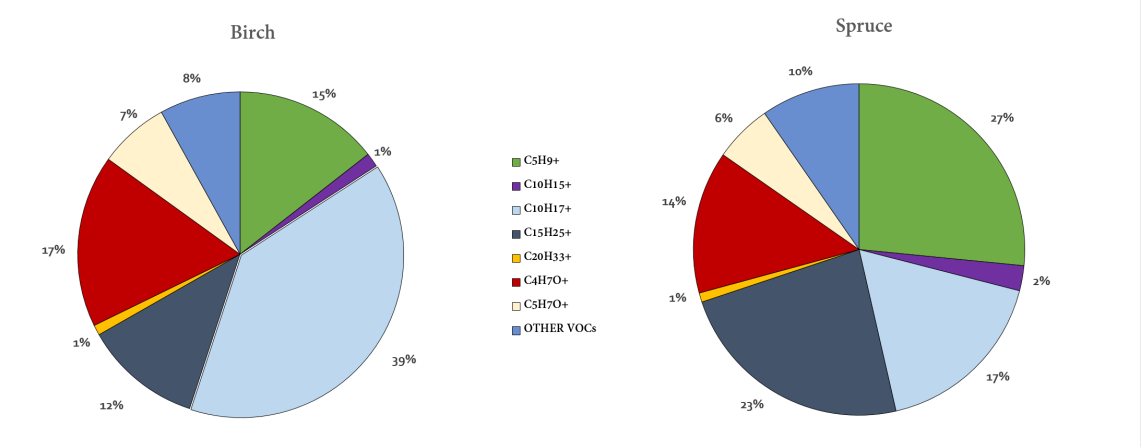

Figure 4.6: Relative contribution of the observed emissions from birch (left) and spruce (right). OTHER VOCs comprises of all oxygenated VOCs except $C_4H_7O^+$ and $C_5H_7O^+$

$C_{20}H_{33}^+$ and $C_{10}H_{15}^+$ is observed to be the least emitted from both the trees having the maximum rate of just 0.005 µg g_{DW}^{-1} h^{-1} and 0.02 µg g_{DW}^{-1} h^{-1} respectively from birch and even a lesser maxima from spruce (Table A.1.). In a study by Hakola et al. (2017), the mean *p*-cymene emission rate during late summer was 0.0005 µg g_{DW}^{-1} h^{-1} while mean α-pinene emission rate was 0.0096 µg g_{DW}^{-1} h^{-1}. Hence, *p*-cymene emissions are an order of magnitude lesser than α-pinene. Similar differences in the magnitude of mean emission rates between $C_{10}H_{15}^+$ and $C_{10}H_{17}^+$ from both trees can also be observed in this study (Table A.1.). However, *p*-cymene is also found to be emitted more than α-pinene from Scots pine, when it is subjected to biotic stress

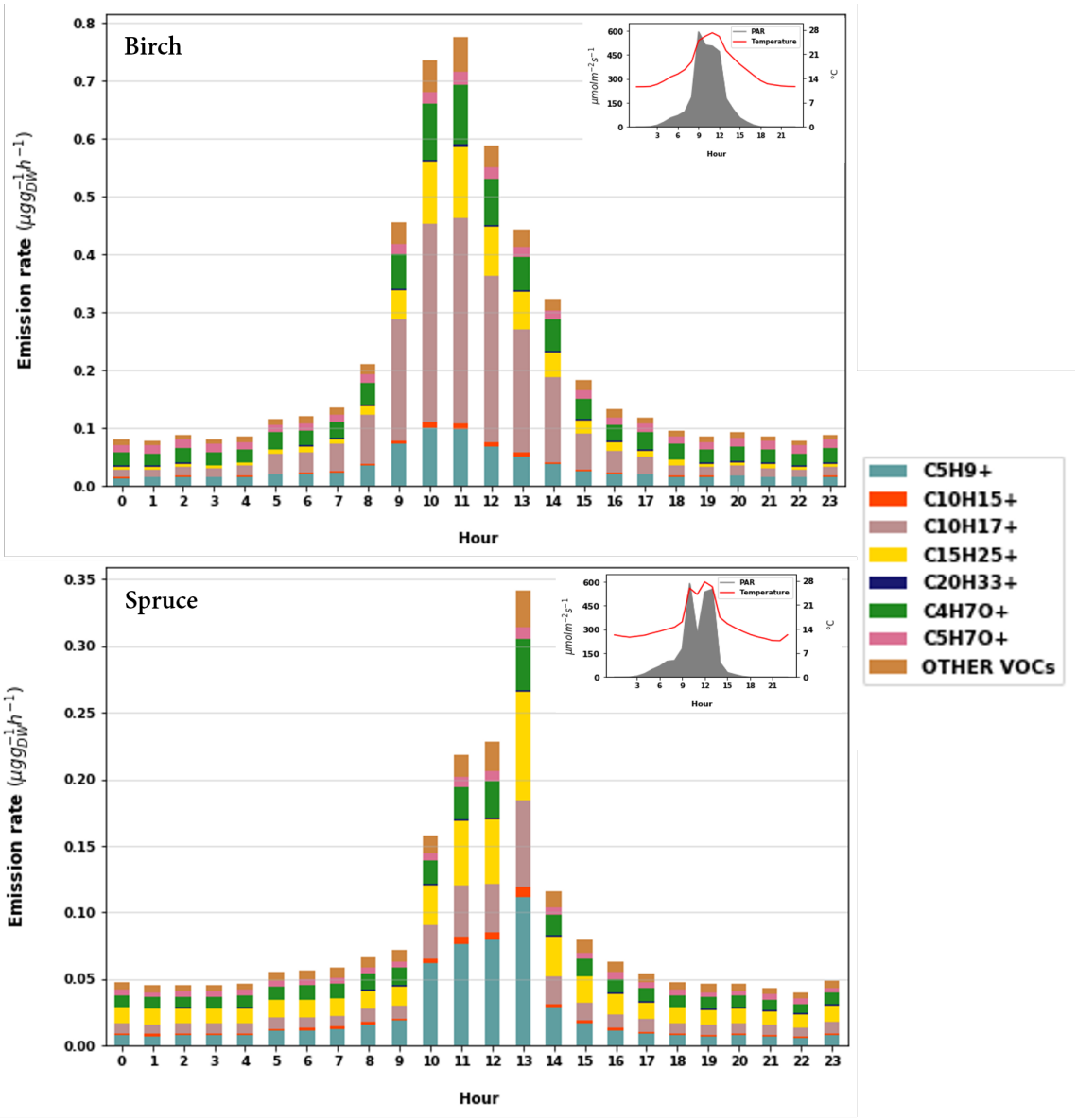

Figure 4.7: Hourly mean emission rates of the observed VOCs from Birch (top) and Spruce (bottom). (Inside) Mean hourly temperature (red lines) and PAR values (grey region) are shown.

(Kari et al., 2019). In this study, $C_{15}H_{25}^{+}$ accounts for 12% of the total observed emissions from birch (Fig.4.6) and the emission rates are less than 0.01 µg g_{DW}^{-1} h^{-1} after 20:00 unlike isoprene and monoterpenes (Fig.4.7). While from spruce, $C_{15}H_{25}^{+}$ emissions are seen to contribute more than $C_{10}H_{17}^{+}$ and are quite comparable to $C_5H_9^{+}$. However, the data set is very small to bring about any decisive results for spruce. While Bourtsoukidis et al. (2013) reflect four to five times more monoterpene

emissions when compared to sesquiterpenes from spruce trees, Hakola et al., 2017 observed higher emissions of sesquiterpenes during late summer from Norway spruce. In this thesis, over the single day of measurement from spruce, $C_5H_9^+$ is known to be the dominant compound, which is followed by $C_{15}H_{25}^+$.

The rest of the VOCs labelled as "other VOCs" in Fig4.6. and Fig.4.7, comprise a combination of oxygenated compounds. The Vocus was able to resolve ions at the same m/z 223 ($C_{15}H_{27}O^+$ and $C_{14}H_{23}O_2^+$). For birch, the peak of sum emissions of all oxygenated compounds except $C_4H_7O^+$ and $C_5H_7O^+$, reached at 11:00, exactly when temperature reached its maxima. Fig.4.7 shows that the sum emissions of all observed compounds are quite constant between 18:00 and 4:00. During this period, the PAR value reaches zero after 18:00 and an evident rise in PAR can be noticed only after 3:00. Since the season is expected to have a strong effect on the emissions, more experiments on long term and short term bases must be conducted in order to gain a better understanding of the emissions of all these compounds especially that of diterpenes and all oxygenated compounds.

4.8 Sources of Error

The major limitations in this study are the lack of sample trees and also the small time-frame. BVOC emission from one tree to another of the same species can vary in terms of quantity and quality. Also, the data in this study do not include emission variation that occur naturally across seasons and hence makes it difficult to quantify the BVOC emissions in a conclusive manner.

The background values were also used in all the analyses which could be another source of error. The background values could not be subtracted as the instrument detected higher concentrations of BVOCs in zero air (filtered air) than sample air, which could have occurred due to contamination. The inability to subtract background values can lead to uncertainties in the analyses and calculation of emission

rates. This might have caused the instrument to detect BVOC concentrations even at night, when originally the emission of compounds from birch could have dropped to zero at night.

Other factors that lead to uncertainties in quantifying BVOC emissions could be due to the sampling technique used. There were large differences between the chamber and ambient temperatures, meaning that the branch did not experience natural conditions when kept in the enclosure and the changes in BVOC emissions did not occur due to natural variations. The surface of the sampling lines can adsorb the heavy and low volatile compounds and cause a reduction in the measured emission rates. There could have been differences in temperature between the chamber and sampling line which could have further led to uncertainties in emission rates of BVOCs. Isolating and heating the sampling line that runs from the chamber to the instrument could solve the temperature difference and adsorption of BVOCs.

5. Conclusion

This is the first study to employ the newly developed Vocus PTR-TOF-MS for characterising and quantifying BVOC emissions from trees. Branch-scale measurements from Downy birch and Norway spruce, two dominant trees of the Finnish Boreal forest, were conducted using the Vocus that have led to the identification of various compounds not observed before in any study concerning birch and spruce. For the first time emissions of diterpenes ($C_{20}H_{33}^{+}$), traditionally considered to be non-volatile, were observed from birch and spruce trees. This is also one of the first studies to observe real-time emissions of oxygenated compounds containing up to 2 oxygen atoms from birch and spruce trees. The quantification of heavy and low volatile compounds could be underestimated as adsorption of these compounds onto sampling tube surfaces might have occurred.

The temperature and light response of terpene emissions from birch and spruce were also observed in this study. Due to the lack of data for spruce, conclusive results for spruce cannot be drawn. The emission potentials of all terpenes for birch obtained in this study are on the lower end of the published results. This might be due to the lowered activity in the the leaves as the emissions were observed during late summer. All BVOC emissions positively correlated with both temperature and PAR. The influence of these two variables on emissions were clearly observed during the measurement period. BVOC emissions were enhanced during at least one of the three days when high temperature and PAR were observed. However, which of the

two had a greater effect could not be discerned in this study. The emissions modelled using the two algorithms also produced similar results without much difference between their correlations with observed emissions. However, only $C_{10}H_{17}^{+}$ emission was better modelled using temperature-light algorithm which could support the fact that monoterpenes from birch are directly emitted after synthesis. Studies have observed similar behaviour with sesquiterpene emissions, but the same could not be confirmed in this study.

This study reveals new insights into the various compounds that are directly emitted from spruce and birch trees. Long term field and stress related experiments in the lab must be conducted to help understand better the emission mechanisms of various oxygenated compounds and also diterpenes which have not been previously observed from these two trees. As birch and spruce trees are common in the Finnish boreal forests, the total emission of these heavy molecules into the atmosphere could be significant and play a vital role in the atmospheric chemistry and physics.

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A. Appendix

Tables

Table A.1: The emission rate (ng g_{DW}^{-1} h^{-1}) summary of $C_5H_9^+$ (isoprene signal), $C_{10}H_{15}^+$ (*p*-cymene signal), $C_{10}H_{17}^+$ (monoterpene signal), $C_{15}H_{25}^+$ (sesquiterpene signal), $C_{20}H_{33}^+$ (diterpene signal) respectively from birch/spruce.

	$\mathbf{C_5H_9^+}$	$\mathbf{C_{10}H_{15}^+}$	$\mathbf{C_{10}H_{17}^+}$	$\mathbf{C_{15}H_{25}^+}$	$\mathbf{C_{20}H_{33}^+}$
Mean	32/23	3/2.1	86/15	26/20	2.2/0.7
Minimum	9.8/4.6	0.97/0.91	7.3/7.7	1/11	1.3/0.5
Maximum	238/136	22.7/8.3	1170/80	351/95	5.5/1.4

Figures

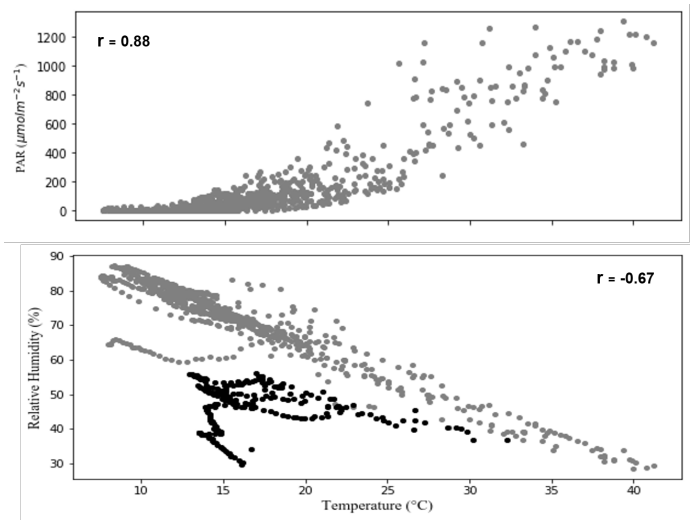

Figure A.1: Photosynthetic Active Radiation and Relative Humidity dependence on Temperature. These are measurements that were observed from the chamber. (Below) The spread in the values observed at around 15°C is due to the decline in water level. Otherwise, an inverse relationship clearly exists between the two.

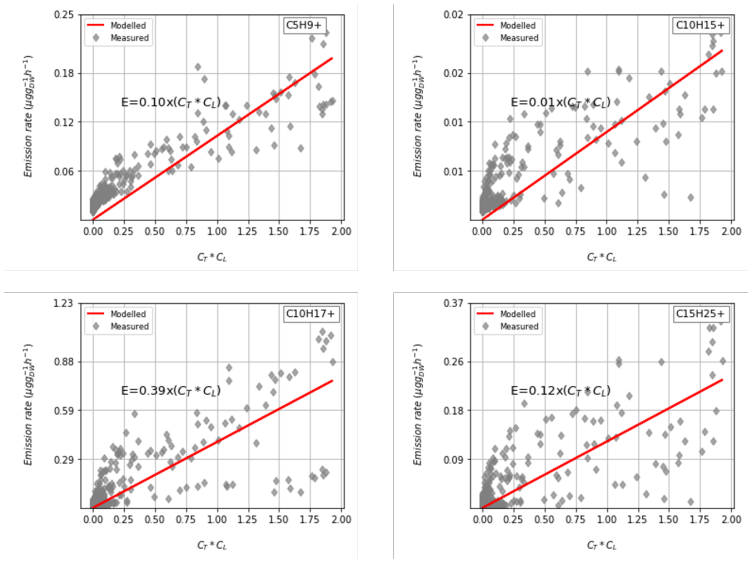

Figure A.2: Emissions of terpenes from Birch modelled using temperature-light algorithm.

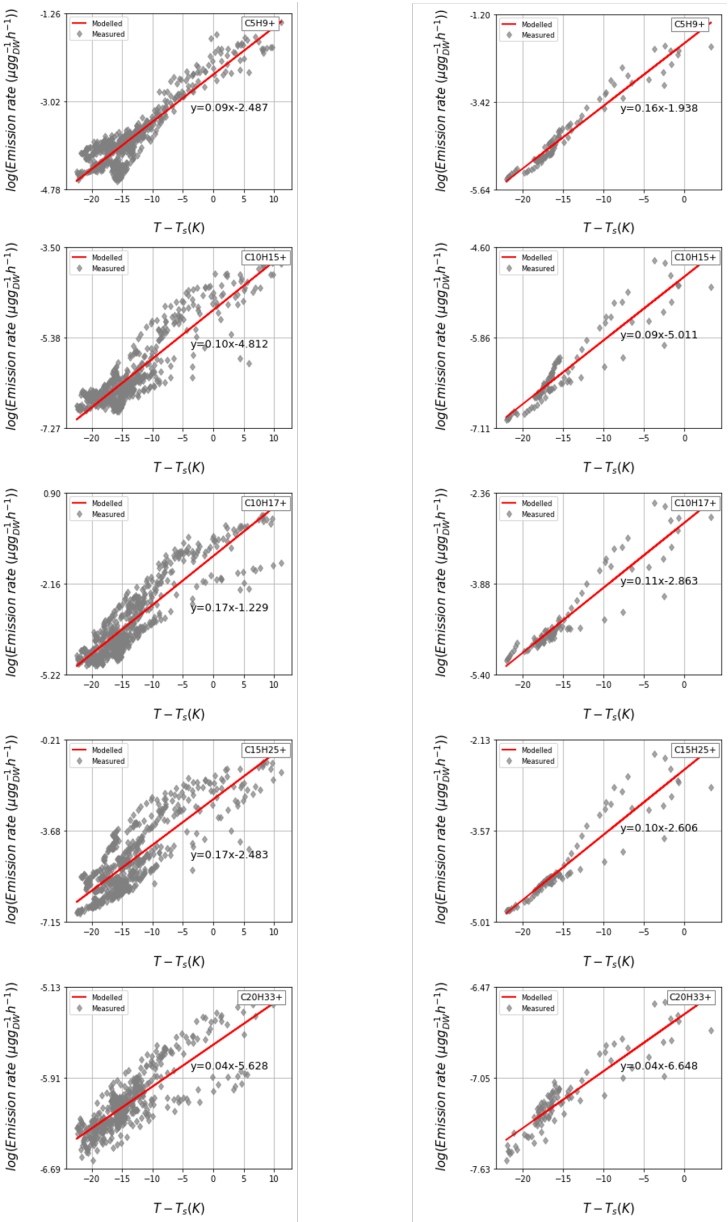

Figure A.3: The emissions of compounds from Birch (left) and Spruce (right) modelled using temperature algorithm.

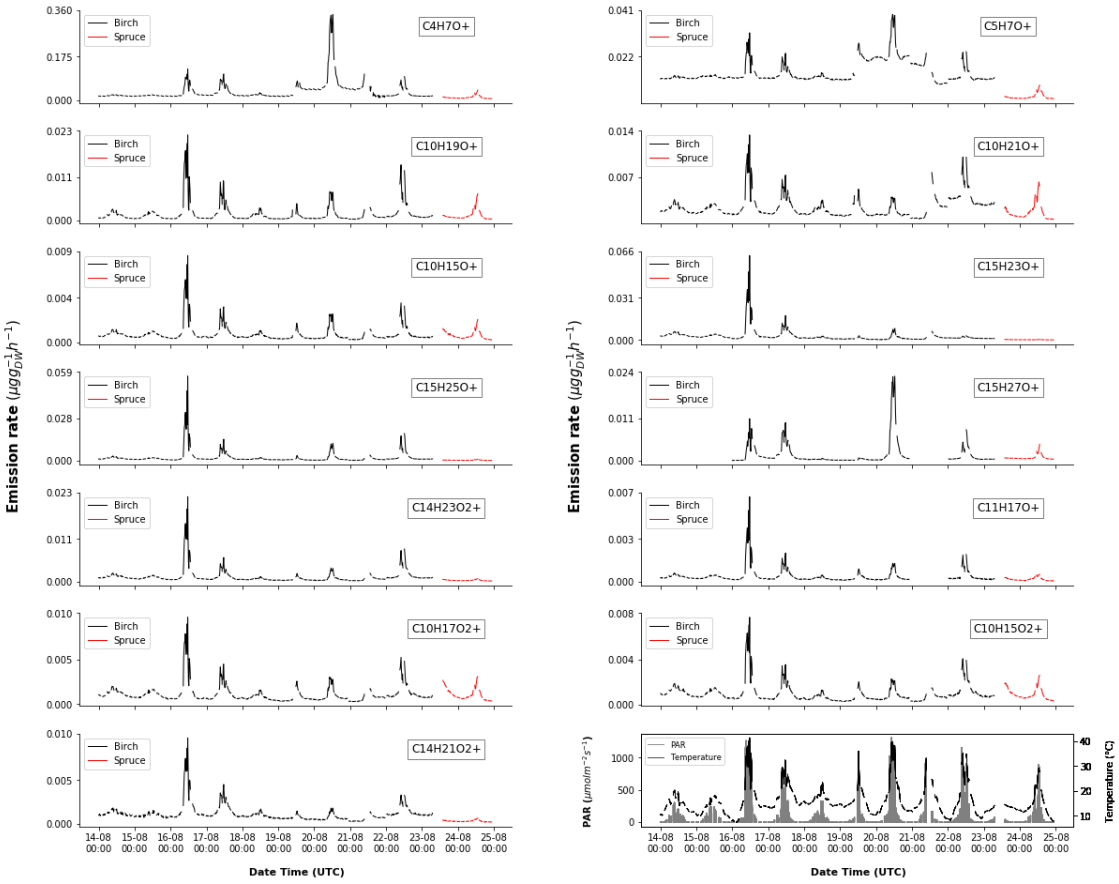

Figure A.4: Emission rates of oxygenated compounds observed from birch and spruce. The red line corresponds to spruce measurements.